Corrosion

CORROSION COSTS

$6,000,000,000.00 ANNUALLY!

No industry escapes ...how much do you pay?

Don't risk needless waste

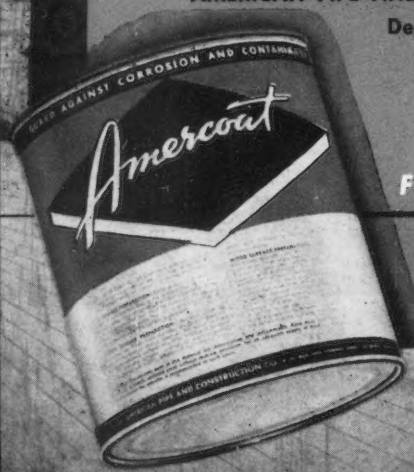
Corrosion damage is bound to occur. The problem is to provide adequate protection. Conventional coatings often fail when attacked by acids, alkalis, salts, gases and atmospheric conditions. As a result, every industry pays a terrific bill—far more than it should. Your own costs, too, may be larger than necessary. Minimize your risk—do these two things now—

1 — Check up on your costs;

2 — Provide adequate protection for danger points.

Experienced and competent Amercoat engineers are available to help you on both. They'll check up on your costs, which may be greater than you know because the effects of corrosion are often hidden. They'll report on conditions as they find them. They'll recommend steps to take if greater protection can be provided and money saved. Inquiries from interested executives will receive prompt attention. There's no obligation—write today.

AMERCOAT DIVISION
AMERICAN PIPE AND CONSTRUCTION CO.
Dept. 2G, 4809 Firestone Blvd.,
South Gate, California



FOLLOW THE LINE OF *most* RESISTANCE

EXAMPLE OF AVOIDABLE LOSS—The coating on this tank broke down under atmospheric conditions because it was not designed to do a protective job—result, useful life of unit greatly reduced and costly replacement necessary.

A SYSTEM OF SURFACE PROTECTION

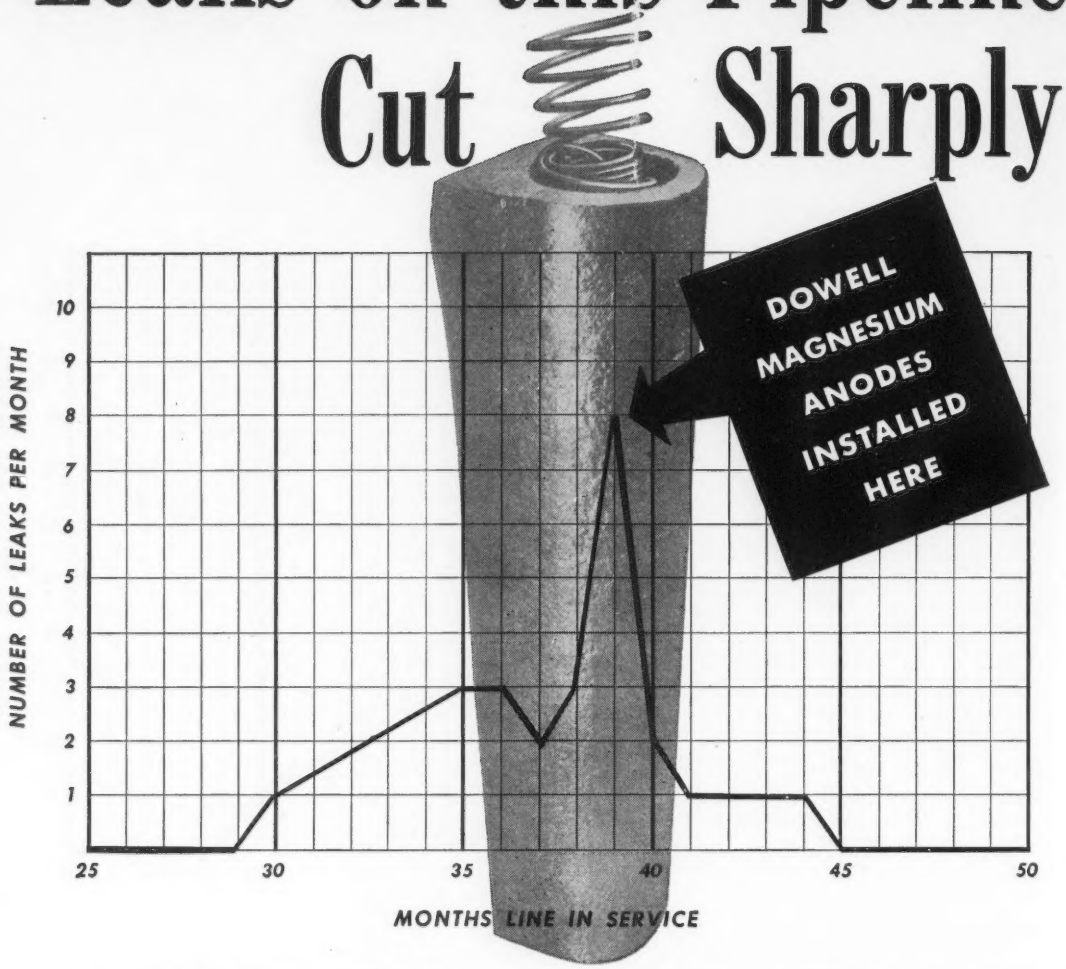
We have coated and wrapped more than 200 million feet of pipe, sizes ½" to 60" both inside and outside (and that's a lot of pipe in anybody's language). Ninety-six (96) of the top hands in the business.

By the addition of more and better equipment, we are ABLE, WILLING AND READY to handle both your new and used pipe jobs. Complete reconditioning services available.

"PUTTING *Permanence* IN PIPE"

MAYES BROS. INCORPORATED HOUSTON

Leaks on this Pipeline Cut Sharply



The graph above shows the dramatic reduction in leak rate that occurred when Dowell magnesium anodes were installed on a 33 mile 8 inch asphalt covered pipe line. This installation saved thousands of dollars in maintenance costs alone, as well as extending indefinitely the time when the line would have to be reconditioned or replaced.

This is an example of the savings that can result when Dowell anodes are used to control corrosion on underground pipelines. The degree of protection afforded will depend upon soil conditions encountered and the number of anodes used. Easily and economically installed on existing pipe lines, Dowell magnesium anodes require no external power and cut maintenance costs to a minimum. Also, Dowell anodes are alloyed to specifications designed for maximum anode efficiency and long life.

A subsidiary of The Dow Chemical Company—pioneer in the use of magnesium for cathodic protection—Dowell offers the technical know-how and extensive research facilities which make it the logical source for magnesium anodes for corrosion control. Write directly to Tulsa for additional information.

DOWELL INCORPORATED
TULSA 3, OKLAHOMA

DOWELL
MAGNESIUM ANODES
GALVO-PAK • GALVO-LINE

SUBSIDIARY OF THE DOW CHEMICAL COMPANY

THIS MONTH'S COVER—Sheets of Saran Rubber Q-187.5 (Dow Chemical Co.) are being applied here to a tank top. Four coats of adhesive are applied to metal before application of the 3/16-inch sheets. Saran, a vulcanized elastomer, has good chemical, oil and solvent resistance, a low degree of swell and low rate of permeation to hydrocarbon solvents. Aging resistance below 187° F. is good. The material also is used extensively for lining pipe and for gaskets.

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Entered as second class matter October 31, 1946, at the Post Office at Houston, Texas, under the act of March 3, 1879.

Corrosion is Indexed Regularly by Engineering Index.

Corrosion

devoted entirely to

CORROSION
Research and Control

Published monthly as its official journal, by the National Association of Corrosion Engineers, Inc., at Houston, Texas, U. S. A., to provide a permanent record of progress in the control of corrosion as described in papers prepared for the Association and from other sources.

Vol. 5 JULY, 1949 No. 7

CONTENTS

	Page
Directory of Regional and Sectional Officers	iv
Technical Committee Activities	xi
TECHNICAL SECTION	
Corrosion Research in the Navy *By Julius J. Harwood and Fred Schulman*	203
Special Anodes for the Cathodic Protection of Water Tanks *By A. L. Kimmel*	217
Development of Pipe Line Coatings and Mechanical Application Methods *By Stephen D. Day*	221
High Temperature Corrosion of Metals *By Andrew Dravnieks and Dr. Hugh J. McDonald*	227
Principles of Writing Specifications for Metal Protective Paints *By W. W. Cranmer*	234
The Role of Adsorption from Solution in Corrosion Inhibitor Action *By Dr. Norman Hackerman and Harold R. Schmidt*	237
Topic of the Month—Destruction of An Admiralty Tube Bundle by Stress Corrosion in the Presence of Mercury *By B. B. Morton*	244
NACE NEWS SECTION	
Deadline on Amendment Ballots July 14	1
North East Region to Vote on Board Members	1
South Central Region News	1
New Corporate and Associate Members	1
Corrosion Short Course Set Sept. 12-16	2
NACE Calendar	2
Region Reports for 1948	3
New Products, Materials, Services	4
Corrosion Problems	5
NACE 1949 DIRECTORY SUPPLEMENT	6
CORROSION ABSTRACT SECTION	
Bearing	9
Coatings	9
Fundamentals	18
Index to Advertisers	25

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The Pipeliner Says, "CORROSION ? An A-No. 1 Headache!"

Two Answers from MIDWESTERN

OWENS-CORNING COROMAT
UNDERGROUND PIPEWRAP

Now Midwestern is stocking the new Owens-Corning COROMAT, an improved underground pipewrap that offers an increase in tensile and tear strength ranging from 200% to 400%. COROMAT is a porous mat of glass fibers reinforced with long, continuous strands of Fiberglas Yarns integrated into the wrap in a multi-directional pattern. This added strength eliminates breakage in application and allows higher wrapping speeds and use of longer rolls. Midwestern's proven service assures prompt delivery from any one of four warehouses located in Tulsa, Houston, Kansas City and Newark.

GLASFAB

GLASFAB, the new hydrocarbon thermoplastic impregnate Fiberglas cloth is now in wide use for hand wrapping "hot spots," field joints, field repairs and for machine-wrapping river crossings and "hot lines." Like Coromat it is impervious to moisture and heat, compatible with coal, tar or asphalt coatings and has good porous characteristics. Also, GLASFAB has a high tensile strength — 92 pounds per inch — and is soft, pliable and non-irritating to the hands. GLASFAB comes in lengths 150-foot to 1200-foot rolls with widths from 2 to 36 inches.

WRITE MIDWESTERN FOR MORE DETAILED INFORMATION

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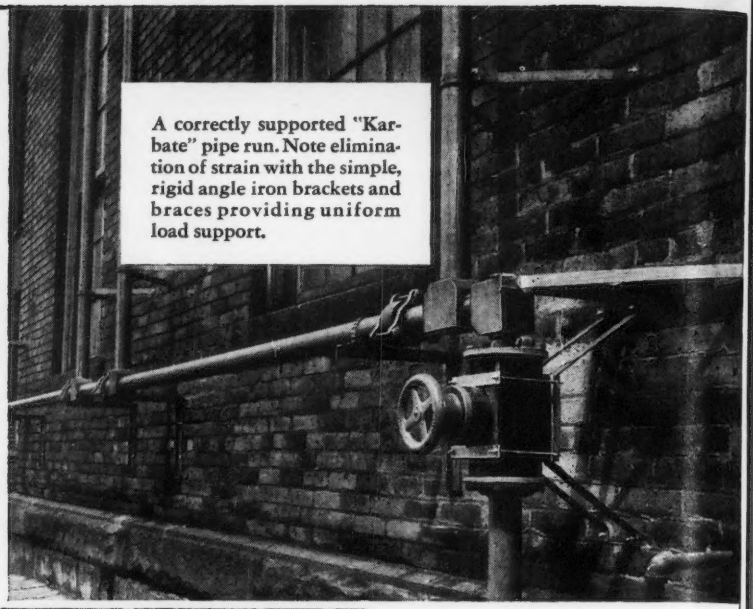
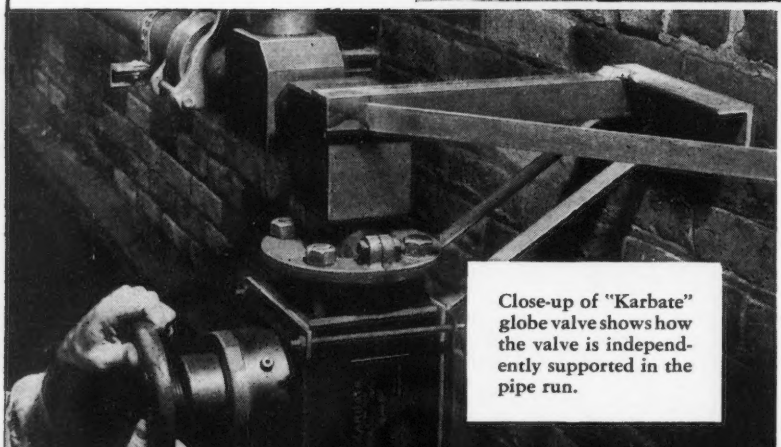
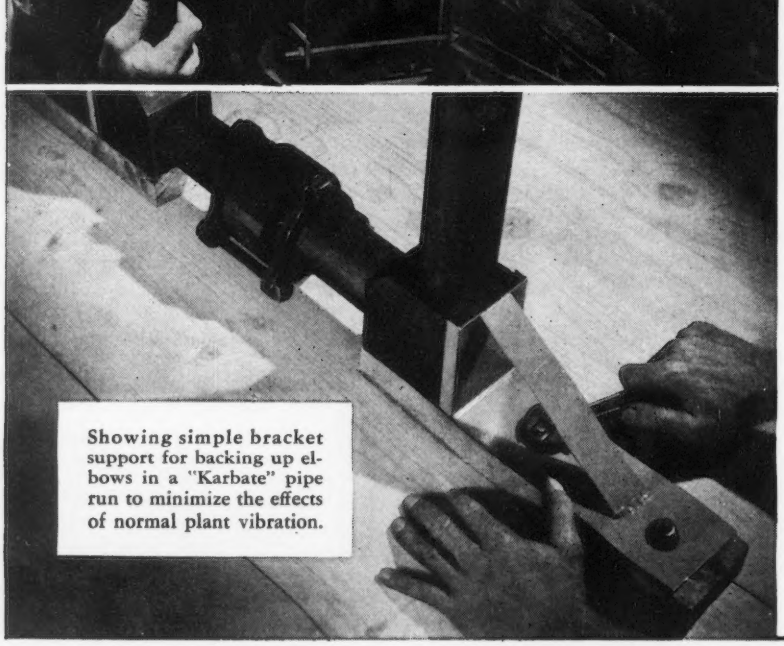
How to support a "Karbate" pipe line.



A correctly supported "Karbate" pipe run. Note elimination of strain with the simple, rigid angle iron brackets and braces providing uniform load support.



Close-up of "Karbate" globe valve shows how the valve is independently supported in the pipe run.



Showing simple bracket support for backing up elbows in a "Karbate" pipe run to minimize the effects of normal plant vibration.

KEEP "KARBATE" PIPE ALWAYS IN STOCK

- Resists the action of acids, alkalies and other chemicals
- Light weight with adequate strength
- Resistant to mechanical shock
- Immune to thermal shock
- Easy to machine and install
- Full range of sizes and fittings

Write for Installation Manual M-8801 A. Address Dept. C.

The term "Karbate" is a registered trade-mark of

NATIONAL CARBON COMPANY, INC.

Unit of Union Carbide and Carbon Corporation

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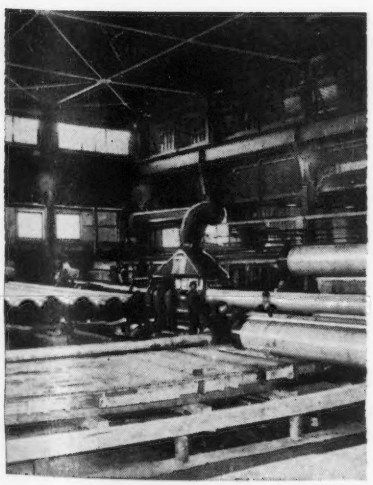
Supervision — PROFESSIONAL APPLICATION OF PIPE COATINGS IN PLANTS AND YARDS

In recent years, there has been increasing recognition of the fact that *proper application* of pipe coatings is a primary requirement of corrosion-proof lines.

This has resulted in an increasing trend towards *professional* coating application in plants and yards where pipe can be delivered and processed under controlled conditions.

Services include: (1) Storing of pipe as received from mill until owner orders it coated and shipped. (2) Indoor application at plants under controlled weather conditions. (3) Warming and drying of pipe before primer application. (4) Cleaning of metal by grit-blasting before priming, followed by drying in ovens. (5) Immediate enamel-coating and wrapping, in thickness and number of coats specified by engineer. (6) Electrical inspection of coating, and repairs if necessary. (7) Protection of coated pipe in transit.

Barrett now offers an expert supervision service in connection with application plants and yards. Owners wishing to avail themselves of the advantages of professional application can have the work done with Barrett materials and under Barrett supervision. We will be glad to supply further information upon request.



THE BARRETT DIVISION
ALLIED CHEMICAL & DYE CORPORATION
40 Rector Street, New York 6, N. Y.

Barrett*

*Reg. U. S. Pat. Off.

SPECIAL PROBLEMS in CORROSION

...and what to do about yours

"ACIDIFIED PECTIN CORRODES OUR EVAPORATORS"

"Grapefruit pectin acidified with hydrochloric acid to a pH from 2.4 to 2.1 is boiled under vacuum," said a citrus products manufacturer. "It corrodes our evaporators. Is there a more suitable metal for them?"

INCO Technical Service made a series of laboratory tests. Here are the results:

	Corrosion rate
Monel	0.0032 ipy†
Inconel	0.0008 ipy
Metal A	0.0021 ipy
Metal B	0.0016 ipy
Metal C	0.0013 ipy

Following the tests, evaporators were constructed of Inconel. They have since proved highly satisfactory.

†ipy — inches penetration per year of continuous exposure.

"WE MUST REDUCE PICKLING CRATE MAINTENANCE COST"

"We clean cast iron parts in a 6% hydrofluoric acid solution at 170° F.," wrote a machine tool manufacturer. "Our pickling crate maintenance costs are too high. Can you help us?"

Two Corrosion Test Spools were prepared and forwarded to this manufacturer with instructions for their use.

The spools were exposed to the corrosive solution for 4 and 28 days, respectively. Corrosion rates were then computed as follows:

	4 Days	28 Days
Monel	0.0008	0.0002
Nickel	0.352	—
Inconel	0.063	0.0678
Metal X	1.098	—
Metal Y	0.880	0.541
Cast Iron	Completely destroyed	

Because of its high resistance to hydrofluoric acid corrosion, Monel was chosen for these pickling crates... maintenance costs were reduced to a negligible amount.

"OUR PROBLEM CONCERNS SATURATION OF LIME SLURRY WITH H_2S"

"What material do you recommend for an absorber unit to saturate a lime slurry with H_2S?" asked a producer of calcium sulfide.

In cooperation with the engineers of this chemical manufacturer, INCO Technical Service made a 46-day test in the plant. This is what they found.

	Corrosion rate
Monel	0.0006 ipy†
Nickel	0.0003 ipy†
Inconel	0.0001 ipy†
Ni-Resist*	0.0011 ipy†
Cast Iron	0.0079 ipy†
Mild Steel	0.026 ipy†

As is evident from these results, Inconel is the most suitable material. It was accordingly recommended as first choice, with Nickel and Monel as alternates.

†ipy — inches penetration per year of continuous exposure.

Quite likely your corrosion problem differs from those on this page.

Even so, the answer to it may be readily available.

The INCO Corrosion Data File contains reports of more than 2,500 tests involving over 40,000 specimens . . . covering all of the commonly used materials including Inco's own products — Monel*, Nickel and Inconel*.

Among these reports, Inco Technical Service may already have the answer to your corrosion problem . . . the solution that can help you speed output . . . save manpower and materials . . . or improve your product.

We invite you to make use of this impartial, valuable service. The first step is to *write today* for a copy of the Corrosion Data Work Sheet.

*Reg. U. S. Pat. Off.

THE INTERNATIONAL NICKEL COMPANY, INC.
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EMBLEM OF SERVICE

INCO TRADE MARK

TECHNICAL SERVICE

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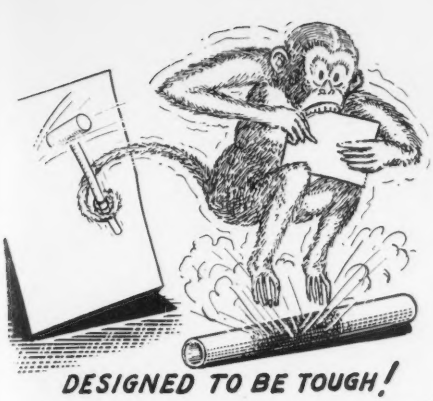
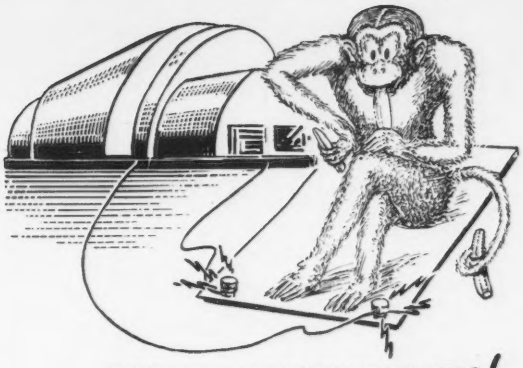


DESIGNED TO BE TOUGH!



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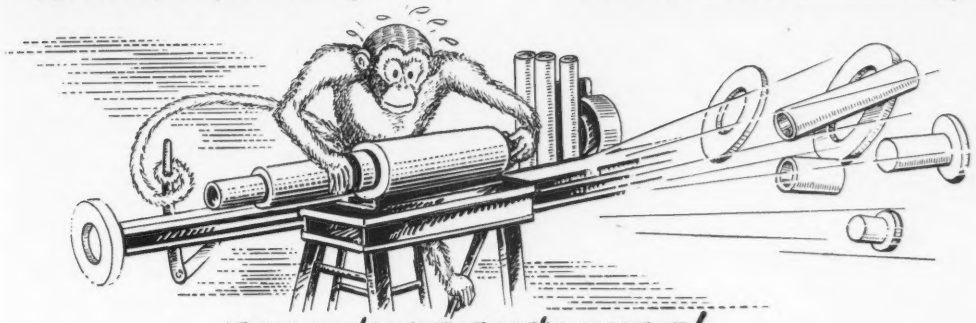

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- Hydrogen Sulphide
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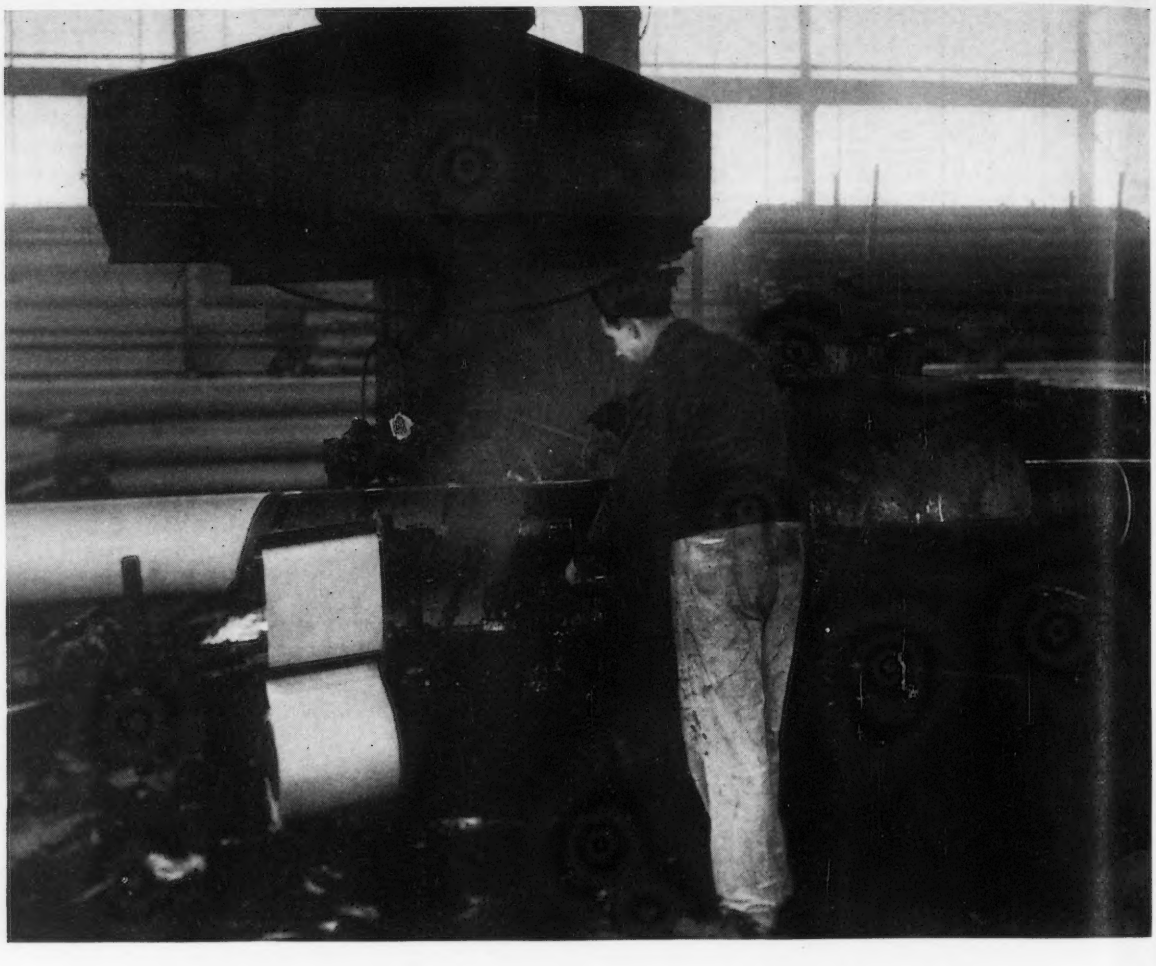

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Tests of Steel, Carbon and Graphite Anodes Now Are Under Way

By M. A. JUDAH*

THE CATHODIC METHOD of protecting underground or submerged metallic structures from its very beginning has presented the problem, among others, of designing and installing suitable and economical ground beds, or anode systems. As the method gained wider usage in industry the problem became increasingly more important. Each interested industry, and many individuals, consequently have constantly directed their efforts toward finding or designing a better and cheaper anode system.

Materials most commonly used for such ground installations have been scrap steel or cast iron. These metals, when buried, usually are back filled with natural soil which is treated in most cases with sodium chloride to reduce the contact and adjacent soil resistances. This treatment reduces the circuit resistance of the cathodic unit involved and consequently lowers the operating power requirement. In some instances sodium hydroxide has been used for the same purposes. This compound, even though more costly than common salt, is considered worthwhile because of its effect, not only in reducing circuit resistance, but also in its ability to make steel and iron surfaces passive to an electric current under certain conditions of solution concentrations. In other words the latter effect serves to reduce the efficiency of electrochemical dissolution of the steel or iron and, as a result, may be expected to increase appreciably the life of the anode installation.

As time went on, other possible materials were considered and tried. As a result, carbon and graphite anodes were found to have an application in the field. As in the case of the metallic type, numerous efforts have been made to improve the life of the carbon and graphite anodes by using special backfills, such as coke breeze, and chemical treatment of the various backfills used. In addition, some work has been done toward determining the effect of current densities on the life of these materials.

During 1946 a group of corrosion engineers held a meeting to formulate plans for a joint study of the anode problem. This meeting resulted in a tentative committee being set up to initiate a testing program on anodes and at the same time the NACE was petitioned to sponsor the work. The national organization honored this request and the Committee on Anodes for Impressed Current, TP-3, subsequently was brought into being. The name of the committee was selected so as to differentiate its title, as well as its activities, from those of the committee having to do with galvanic anodes.

At present the committee is made up of representatives from manufacturers and the oil and gas industry. Operating companies have cooperated in making test installations of ground beds and assembling data for study by this group. Several test installations now are under study. All of these locations have anodes of steel, carbon and graphite with various backfills. In addition, some of the backfills are treated with chemical compounds. Results of these tests should make possible definite comparisons among the three materials with respect to their relative values as anodes and also give some indication of the relative merits of the various backfill combinations.

It is believed that work of TP-3 so far has in no way covered all possible phases of the anode problem. Further, it is expected that membership of the committee will be increased as other companies and individuals indicate an interest in the work and are willing to assist in the joint effort. The first interim report of this committee now is in process of preparation for publication. The committee will at all times welcome helpful suggestions and any concrete data which will be of benefit to the industry as a whole.

* Secretary, NACE Technical Practices Committee TP-3, on Anodes for Impressed Currents.

THE NATIONAL ASSOCIATION OF CORROSION ENGINEERS

is a non-profit, scientific and research association of individuals and companies concerned with corrosion or interested in it, whose objects are:

(a) to promote scientific research in determining the causes of corrosion and methods of its control with respect to theory and practice.

(b) to provide a means of exchange of knowledge and ideas among those individuals actively engaged in the control of corrosion.

(c) to promote methods of control of corrosion.

(d) to promote standardization of terminology, methods, equipment and design in the development of methods of corrosion control.

(e) to foster cooperation between individual owners of metallic structures in the solution of their joint corrosion problems.

It is an incorporated association without capital stock, chartered under the laws of Texas. Its affairs are governed by a Board of Directors, elected by the general membership. Officers are nominated by (1) the Board of Directors, or (2) a quorum of at least 25 members, and elected by the membership.

Inquiries regarding membership, and all general correspondence should be directed to the Executive Secretary at the administrative headquarters of the National Association of Corrosion Engineers at 905 Southern Standard Building, 711 Main Street, Houston 2, Texas.

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Corrosion Research in the Navy ★

By JULIUS J. HARWOOD* and FRED SCHULMAN**

CORROSION HAS been aptly termed a "major industry in reverse—all loss with never a profit." The annual loss to the economy as a result of environmental and chemical attack has been estimated to be 3½ billion dollars, truly a staggering figure. This drain upon national resources lately has received intensified attention as a result of the experiences of the last war and the necessity for conserving the limited supply of common structural materials.

Corrosion of metals, of which the most familiar example is the rusting of iron and steel, is obviously a problem of national importance. The chemical, metallurgical, mining, power, oil and fuel industries all are vitally concerned. The use of higher pressures and higher temperatures as a result of technological and scientific advances has increased many times the problems of corrosion. Materials which formerly were considered corrosion-resistant for a specified set of operating conditions have become relatively useless as service requirements become increasingly severe.

Of all the industrial and military activities concerned with the destructive effects of corrosion phenomena, the Navy may be considered to be the most seriously affected. The necessity of maintaining the fleet and air arms of the Navy in operational readiness, while they constantly are exposed to the pernicious influence of a natural agent of corrosion (sea water) and confronted with almost every other known type of corrosion phenomena as a result of the multitudinous service operations and processes aboard ships and aircraft, makes corrosion a most serious consideration in the design of equipment and the selection of materials for naval applications.

Compared to the enormous cost of corrosion destruction, relatively insignificant sums have been expended for the scientific study of corrosion. Much of this necessarily has been in applied research, trouble shooting, evalutation and testing, aimed primarily towards the empirical development of corrosion-resistant alloys, protective coatings, corrosion inhibitors and rust preventatives. Relatively few investigations have concentrated on the fundamentals of corrosion. The authors feel secure in saying that the corrosion and surface chemistry program of the Office of Naval Research, in conjunction with related and supporting ONR projects, represents one of the leading corrosion research programs in this country devoted to the understanding of why metals do or do not corrode and the mechanisms and kinetics of corrosion reactions.

★ Voluntarily Submitted for Publication 27 May 1949.

* Metallurgist, Materials Branch, Office of Naval Research, Department of the Navy, Washington, D. C.

** Chemist, Chemistry Branch, Office of Naval Research, Department of the Navy, Washington, D. C.

The Office of Naval Research, established by an Act of Congress in August 1946, is charged with the overall responsibility for the Navy's scientific research program. For the past three years, ONR has been sponsoring a broad, long-range program in fundamental research covering practically all branches of the physical, biological and naval sciences. This program is executed largely by means of research contracts with academic, industrial, private and government institutions. Equally important functions are the coordination of the scientific research effort throughout the Navy and the dissemination of research information resulting from such endeavors.

The Office of Naval Research corrosion research program, which is jointly administered by the Metallurgy and Chemistry Branches, is aimed at the study and elucidation of the fundamental mechanisms and kinetics of corrosion reactions, and supports the more practical and applied studies underway in the various naval bureaus and laboratories. The object of this article is to describe the ONR corrosion research program and its objectives and to review briefly the progress to date. However, before discussing this program in detail, it may be advisable to describe briefly the prevalent types of corrosion encountered throughout the navy and the general methods currently employed to control them.[1]

Corrosion Types Described

Corrosion is defined as the destruction of a metal by chemical or electrochemical reaction with its environment. Practically all metals and their alloys corrode, the major difference being the degree and rate at which the corrosion process occurs. The science of corrosion may be traced to the 1830's when Faraday enunciated his now famous Laws of Electrochemical Action, but it was not until the early part of the twentieth century that the electrochemical nature of most corrosion processes was recognized definitely. The establishment of the electrochemical mechanism of corrosion on a quantitative basis is a result of relatively recent fundamental research. Electrochemical corrosion occurs when current flows between anodic and cathodic areas situated at different parts of the metallic surface. Obviously all chemical changes involve electron displacements, but the term "electrochemical corrosion" is reserved for current flow over finite distances longer than interatomic spacings. It must be recognized that not all corrosion processes are electrochemical in nature (e.g., simple acid attack), although by far the greatest percentage occurs as a result of electrochemical action. Electrochemical corrosion, resulting from

anode and cathode reactions, may be caused by dissimilar metallic contact, impurities and other metallic non-homogeneities, solution concentration effects and differential aeration currents.

Types of Corrosion

The most common type of corrosion, uniform attack or general corrosion, represents the greatest destruction of metal on a tonnage basis. Failure generally is the result of a decrease in section thickness as a result of uniform chemical or electrochemical attack over the entire exposed surface. This type of attack, because of its characteristics, can be controlled by suitable choice of methods described below, and its progress followed easily, thus enabling reliable service life predictions and adequate design thereof. The other types of corrosion to be discussed are more insidious in nature, difficult to predict and often responsible for unexpected and sudden failure.

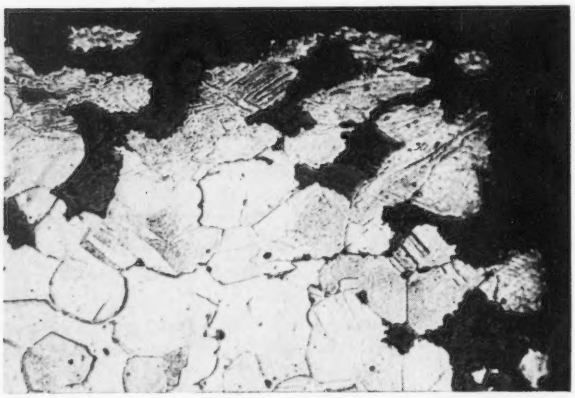

Figure 1—Photomicrograph showing preferential corrosion of beta phase along grain boundaries of alpha brass.

Intergranular or Intercrystalline

Intergranular or intercrystalline corrosion consists of localized preferential attack at the grain boundaries of metals or alloys. Nickel-chromium stainless steels (e.g., 1808) are particularly susceptible to intergranular corrosion when in a "sensitized" condition because of improper heat-treatment, improper welding procedures, or insufficient carbide stabilization. Many of the brass alloys, extensively used throughout the Navy for condenser systems and numerous other applications, aluminum and magnesium alloys, and nickel, are also susceptible to attack of this nature in many environments.

Pitting

Pitting is one of the most destructive and insidious forms of corrosive attack. Although the overall weight loss might be very slight, failure often will occur because of severe localized penetration. Pitting is recognized readily by the presence of pits due to holes, generally localized in isolated areas.

Chlorides, a principal constituent of sea water, are major pitting agents, which obviously makes this type of attack a major problem to the Navy. However, fresh water also will cause pitting in many metals.

Pitting generally is attributed to a lack of homogeneity in the metal surface. Impurities, scratches,

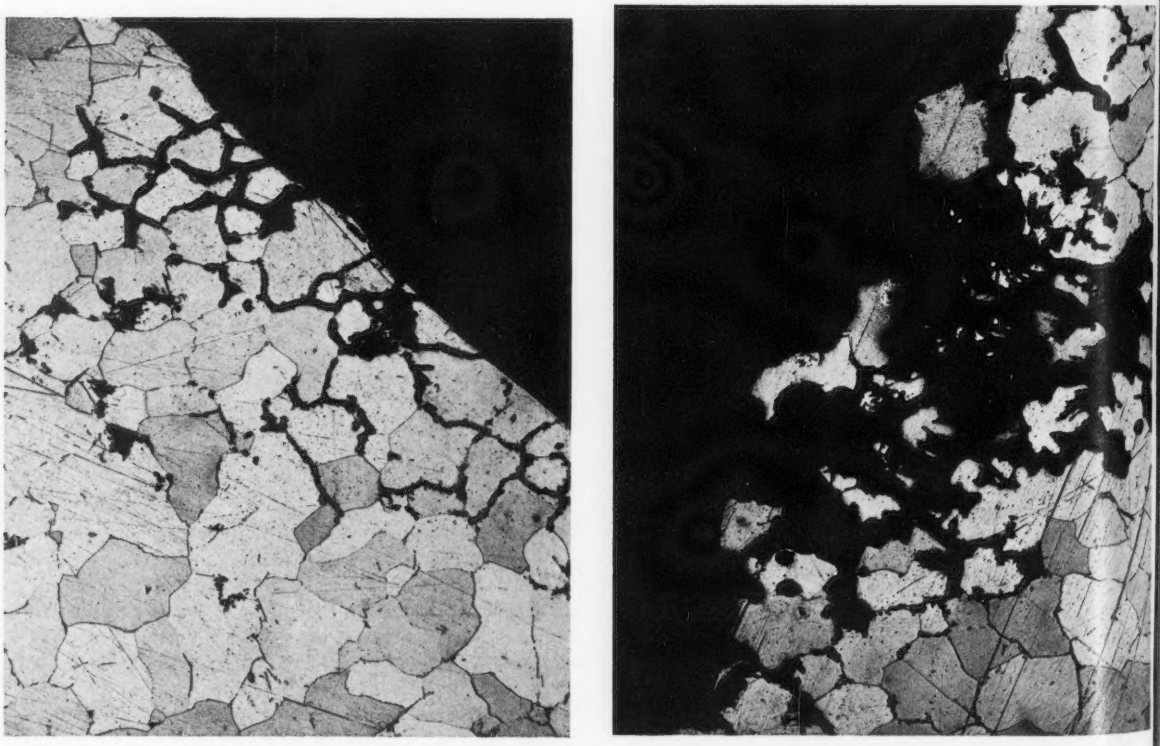

Figure 2—Photomicrographs of an aluminum alloy casting showing severe corrosion and penetration. Note the complete separation of grains.

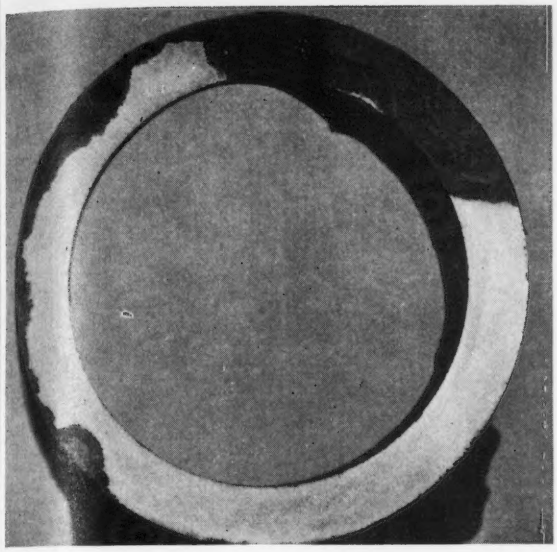

Figure 3—A cross section of a brass pipe which has been buried underground revealing the nature of dezincification. In some areas, it has progressed completely through the pipe wall.

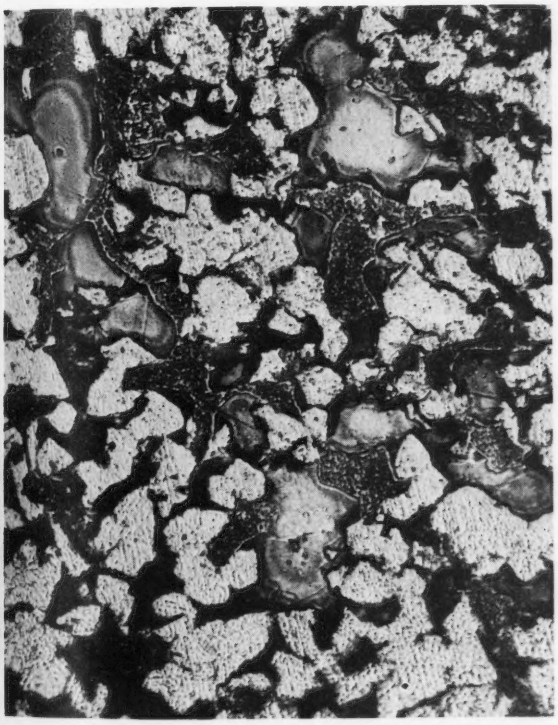

Figure 4—Photomicrograph of one of the dezincified areas of Figure 3 showing islands of the original alpha brass in a matrix of porous copper.

and surface roughness all may promote formation of pits. Pits may form under corrosion products which exist on the metal and also may be promoted by local breaks in "passive films" which form on metal and alloys. Once pitting starts, its progress continues at an accelerated rate. Pitting also may result from impingement or cavitation erosion (described below).

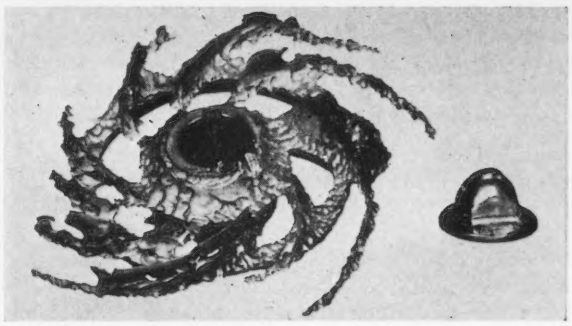

Figure 5—Destructive action of erosion-corrosion on stainless steel pump impeller. (Courtesy Dr. M. G. Fontana.)

Figure 6—Impingement attack on elbow in steam line. (Courtesy of Dr. M. G. Fontana.)

Dezincification

Dezincification, a phenomenon which formerly caused considerable equipment failures aboard ship and is still a problem, usually is observed in the copper-zinc brass alloys. The net result of dezincification is a selective removal of the zinc, leaving as a remainder a weak, spongy, copper structure.

The exact mechanism by which dezincification occurs is still a matter of dispute. Two schools of thought exist: one claiming the entire alloy goes into solution with the redeposition of copper and the other upholding the selective leaching of zinc with the copper remaining in situs. Dezincification is observed readily by the change from the yellow color of brass to the distinctive copper color. It may occur as a uniform attack over the entire exposed area or as a plug type attack in localized areas. Dezincification of brasses results in a severe loss of strength and ductility and occurs most often in sea water or aerated liquids. Control of dezincification has been accomplished in some measure by the addition of

small amounts of tin, arsenic or phosphorous to the various brass alloys. Lately the copper-nickel alloys have been substituted for the copper-zinc series so this type of corrosion is no longer as troublesome and costly to the Navy as it was.

Erosion-Corrosion

Erosion-corrosion, another major destructive attack encountered in Naval service, is the result of the combination of corrosion and mechanical action. Turbulence, fluid impingment, suspended solids and other mechanical and abrasive factors greatly accelerate corrosion rates. Some examples of equipment that are especially subject to this type of attack will emphasize the serious nature of the problem: pumps, valves, agitators, pipe lines, heat exchanger tubes and propellers all are susceptible.

If it is realized that most metals and alloys depend upon some sort of protective surface (oxide film, corrosion product, coatings) for corrosion resistance, then it easily is seen that destruction of these surfaces by mechanical action and the continuous exposure of fresh metal will result in a rapid deterioration. One type of erosion-corrosion attack often encountered in naval vessels is impingement and cavitation corrosion.

Impinging streams of water containing entrained gases (bubbles) and cavitation effects, a consequence of the damage resulting from the formation and collapse of cavities in the liquid at a solid-liquid interface, cause particular difficulties with corrosion of ship propellers. Concentration cell effects are associated closely with this type of attack.

Galvanic Corrosion

Galvanic corrosion is the best illustration of truly electrochemical corrosion and is responsible for many of the major corrosion problems. In a broad sense, it includes many of the other corrosion types. The electrochemical contact of two dissimilar metals in an electrolytic medium will result in a potential difference between the two, and a flow of current will occur. Such dissimilar metallic contacts commonly occur where fasteners, bolts, nuts, and screws are used, or when porous metal coatings are applied. The electrochemical reactions occurring at these metal electrodes result in accelerated action at one metal and decreased action at the other as compared to their open circuit corrosion behavior.

The familiar Electromotive Force Series is often useful in predicting the approximate behavior of such reactions. The metals high in the series (base metals-anodic) are less corrosion resistant than those at the bottom (the noble or cathodic metals). However, surface conditions such as oxides, gas films, or other passive films, often cause deviations from "standard" potentials, and unless the EMF series is intelligently used it may lead to erroneous interpretations.

Galvanic corrosion usually occurs as localized attack near the points of contact and may cause rapid failure though little corrosion is found elsewhere. Galvanic

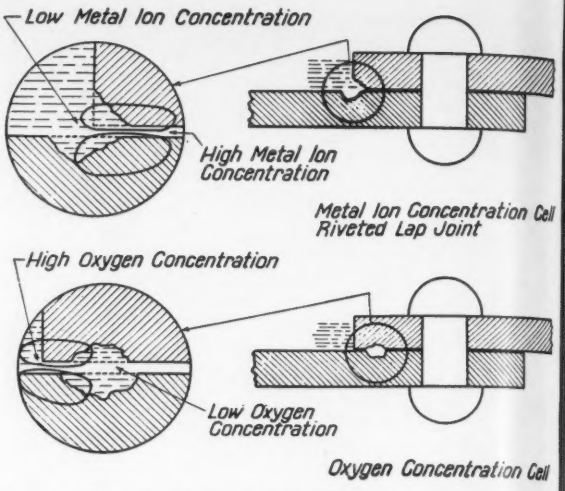

Figure 7—Diagrams showing typical condition for concentration cells. (The International Nickel Co., Inc.)

corrosion or couple action also may occur as a result of the existence of local cells due to the presence of impurities, surface inhomogeneities, and concentration cell effects. The principles of galvanic corrosion often are made use of in combatting corrosion by cathodic protection (described in greater detail subsequently). The effects of galvanic corrosion may be minimized by using combinations of materials with similar electrode potentials in the medium in which they will be exposed; insulation of joints; ensuring that the noble metal has a smaller area than the metal subject to attack (anode); painting both metals or the noble metal by itself.

Concentration Cells

Concentration cell corrosion, a type somewhat similar to that just discussed, occurs when one metal is immersed in, or in contact with different concentrations of its environment. Localized attack occurs in a manner similar to that of galvanic corrosion. Metal ion concentration cells or oxygen concentration cells, which may exist simultaneously, are both well known types. This type of corrosion often is associated with crevices, scale and surface deposits.

Stress-Corrosion

Stress-corrosion or accelerated corrosion resulting from the combination of corrosion and stress, either internal (residual) or externally applied stresses, is probably the least understood of all corrosion mechanisms. The well known "season-cracking" of cartridge cases and caustic embrittlement of steam

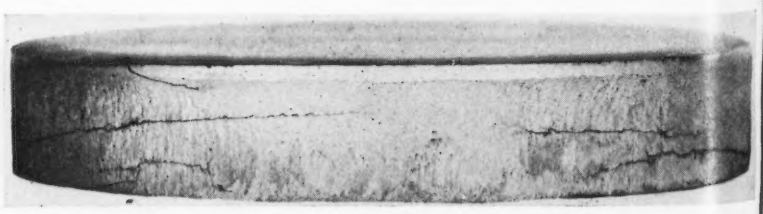

Figure 8—Stress-corrosion cracks in brass disk ("season-cracking").

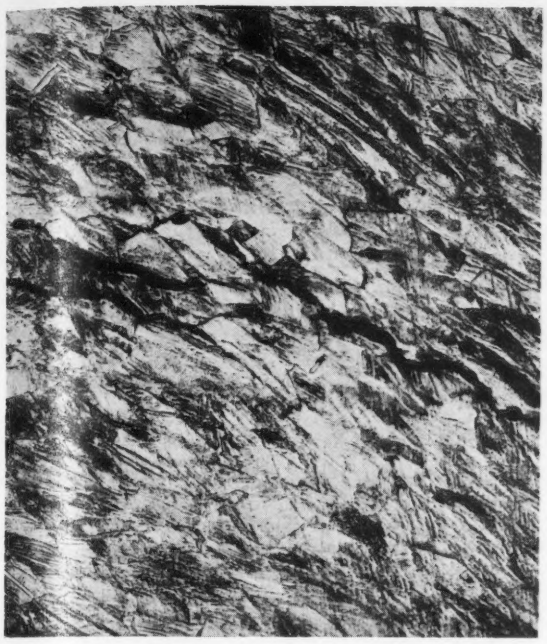

Figure 9—Photomicrograph in area of one of the cracks on Figure 8 showing intergranular nature of crack.

Figure 10—Photomicrograph of brass specimen which underwent severe stress-corrosion showing intergranular nature of cracks.

boilers are familiar examples of this type of corrosion. Stress-corrosion manifests itself by the formation of cracks along localized paths, generally intercrystalline in nature, although in some alloy systems they may be transcrystalline.

There is no universally accepted mechanism of stress-corrosion although it generally is supposed to be electrochemical in nature because of the existence of microstructural anodic and cathodic areas. These local cells may result from a difference in chemical composition between the grain boundaries and the interior of the grain or from local stress (strain) conditions. High zinc-brasses, aluminum alloys and stainless steels are susceptible to stress-corrosion. Once attack occurs, the presence of stress accelerates the corrosion to a marked degree. Stress-corrosion is a most insidious type of attack. It often is not detected until failure occurs. Factors influencing stress corrosion are degree and nature of stress concentration, nature of corrosion environment, temperature and internal-metal structure. Stress-corrosion often may be prevented by stress-relieving heat treatments, use of protective coatings, surface compressive stresses, cathodic protection and proper design of equipment.

Corrosion-Fatigue

Corrosion-fatigue, another problem extensively experienced in naval applications, is similar to stress-corrosion in that it is a combination of stress and corrosion. The damaging effect of the simultaneous action of corrosion and cyclic stresses on metals often is greater than the sum of the individual damage arising from cyclic stresses and corrosion. Corrosion-fatigue progresses through the formation of deep, sharp pits which become the origin of cracks and subsequent failure.

Often associated with corrosion-fatigue is the rapid corrosion that occurs at the interface between contacting, highly-loaded metal surfaces subjected to slight relative (vibratory) motions known as fretting corrosion. It is characterized by deep pits and surface discoloration. Because it affects loaded surfaces, its effects frequently are catastrophic. As higher stresses in machine parts are employed, frequent trouble from fretting corrosion may be anticipated.

High Temperature Corrosion and Oxidation

A type of corrosion which is becoming increasingly important to the Navy is high temperature corrosion and oxidation. As with all other chemical reactions, an increase in temperature results in a similar increase in the rate of corrosion, as well as introducing other concomitant factors. High-temperature oxidation or high-temperature reactions with sulfur and the halogens may, at first glance, seem to be simple chemical combination reactions. However, it now is clearly recognized that oxidation and tarnishing are electrochemical phenomena. Metal ions have been demonstrated to diffuse outward through the oxide (sulfide or halide) film as well as the less frequent diffusion of reactant (gaseous) ions inward. A growing film may be compared to a current-producing cell with the metal-film interface (as anode) supplying cations and electrons for outward diffusion and with the attacking substance-film interface (as cathode) supplying the anions for inward diffusion. The film acts as both the internal and external circuit of a closed cell.

Methods of Control

As a result of the destructive effects of the corrosion phenomena described above, numerous methods of corrosion control have been developed empirically to facilitate the practical and satisfactory service application of metals and alloys. The choice of control method to meet a specific corrosion problem is determined by the economics involved, feasibility of control application and the intended service life. Several methods to control and prevent corrosion are described below.

Cathodic Protection

As previously mentioned, one method extensively utilized for the prevention of corrosion or for minimizing the rate of corrosion makes use of the basic principles of galvanic corrosion. Cathodic protection is accomplished by supplying a flow of current to a metal surface, either by means of a galvanic coupling or by an external current source such that the electrochemical corrosion reactions, operating because of local cells on the surface, either are stifled or neutralized. Cathodic protection thus may be divided into two general classes: protection by the use of sacrificial anodes or protection resulting from impressed currents. Galvanized (zinc-coated) steel is a most familiar example of cathodic protection utilizing the metallic zinc coating as a sacrificial anode. At any break in the zinc coating which is in contact with the corrosion environment, current is generated by the zinc-iron galvanic cell. The current flow is such that zinc is the anode and corrodes preferentially, cathodically protecting the steel. Any bare spots on the steel surface will be protected by the surrounding areas of zinc. Sacrificial external anodes of zinc and magnesium are widely used to protect buried pipe lines and hot and cold water tanks. The Navy makes use of similar methods to protect ship and submarine hulls, aircraft and ballast tanks.

An impressed current from an external source accomplishes the same results by neutralizing the local currents produced by the numerous local cells existing on the surface. The applied current enters into the metal over the entire area in a direction opposite to the local cell currents and thereby minimizes corrosion.

Metallic Coatings

In addition to metallic coatings used for cathodic protection, non-sacrificial metallic coatings (e.g., copper or nickel on iron) are often employed to serve as physical barriers to the corrosive environment. However, such non-sacrificial coatings must be well bonded to the base metal, dense and free of pores in order to afford effective protection. If breaks exist in the coating, electrolytic action will occur at the local cells and the current flow will serve to increase corrosion of the base metal, since the latter is anodic to the coating. The type of corrosive medium or environment is most important. For example, aluminum is cathodic to iron in fresh water and can be used as a protective coating only if pore free, but in sea water the aluminum reverses its potential and acts as a sacrificial anode, cathodically protecting the iron. Temperature is also important, since polarity reversals have been noted with temperature changes, zinc being a well known example. Thus, again it is essential to emphasize the limited utility of the Electromotive Force Series in predicting the galvanic behavior of metal couples in various corrosion environments.

Non-Metallic Coatings

Non-metallic coatings, including paints, lacquers, organic and inorganic coatings, serve largely to isolate the metal from the corrosion environment and limit diffusion of both moisture and oxygen. They often are used in conjunction with cathodic protection and inhibitors.

Organic inhibitors are believed to afford corrosion protection by adsorbing on the metal surface and forming a tightly bound mono-molecular film or monolayer of ions. These inhibitors alter the surface potential slightly and function by diminishing the rate at which hydrogen ions or other ions can reach the metal surface. Passivators (e.g., red lead and zinc chromate), on the other hand, function by making the potential of the metal in contact with the solution more noble. It has been postulated that they strongly adsorb on the metal surface and satisfy secondary valence forces, thus diminishing the reactivity of the metal. Passivators are characteristically oxidizing compounds or strong electron adsorbers. Vapor phase organic inhibitors and rust preventatives recently have been developed in an effort to expand Naval use of inhibitors to control corrosion of equipment.

Oxide coatings, ceramic coatings, rubber, glass and phosphate coatings are also examples of non-metallic coatings which are protective.

Deaeration of the liquid environment also has resulted in markedly reducing corrosion losses in boilers, condenser systems and other similar apparatus. Alterations of the corrosion environment by other suitable means may also result in effective corrosion control.

Purification of Metals

Metal purification has successfully improved the corrosion resistance of aluminum and magnesium. The removal of minor detrimental impurities, such as iron and nickel, from magnesium has markedly increased its corrosion resistance such that pure magnesium is virtually unattacked by sea water. Purification reduces the number of local cells and consequently avoids galvanic action. In the case of iron, where the amount of oxygen in solution is important and oxygen concentration cells may be present, purification has not resulted in a great improvement in corrosion resistance to sea water.

Alloying for Chemical Resistance

Alloying for chemical resistance is a popular means for obtaining corrosion control. The applications of stainless steel, Duriron and other corrosion-resistant alloys are too well known to go into further detail. The mechanism of their corrosion resistance, however, is of great theoretical and practical importance. The "passivity" of these alloys is, and has been, a subject of much research and will be discussed further in subsequent paragraphs. Alloying also has been of great value in the development of oxidation-

resistant materials capable of withstanding high temperatures.

One other important method of providing control of corrosion is the utilization of adequate equipment design. Proper care in design to avoid crevices and concentration cells, opportunities for stagnant areas, high localized stress areas, hot spots, and to insure proper drainage and surface contouring will do much to retard avoidable corrosion and improve equipment life and operating costs.

It is not to be considered that the corrosion reactions and methods for their control discussed above are unique to the Navy. They are encountered in many other industries and operating environments. The experiences and practices encountered elsewhere have been of tremendous value in assisting corrosion control throughout the Navy and obviously the reverse is also true.

Section II

In order that the corrosion projects and problems currently being studied under Office of Naval Research sponsorship may be feasibly discussed, the overall program arbitrarily has been classified into the following general groupings:

1. Passivity and Film Formation Studies.
2. Inhibitor and Passivator Studies.
3. Galvanic Corrosion Studies.
4. General Corrosion Studies, and
5. High Temperature Oxidation and Corrosion Studies.

Passivity and Film Formation

Most metals and alloys depend upon the formation of protective surface films (passivation) for sucessful use under corrosive conditions at normal and elevated temperatures. Breakdown of these films results in corrosion failure. It is obvious, therefore, that a knowledge of the mechanisms of passivation and the factors influencing the formation, nature and breakdown of protective films is essential to the complete understanding of corrosion phenomena and the explanation of why metals do or do not corrode. Since the time of Faraday, the phenomenon of passivity has been the subject of a great deal of experimentation and speculation with no completely acceptable theory proposed. The recent issue of the CORROSION HANDBOOK defines passivity in the following two ways: "A metal or alloy active in the EMF series is considered passive when its electrochemical behavior becomes that of an appreciably less active or noble metal"; or "A metal or alloy is passive if it substantially resists corrosion in an environment where, thermodynamically, there is a large free energy decrease associated with its passage from the metallic state to appropriate corrosion products."

At the present time two theories of passivity predominate. One, The Generalized Film Theory attributes passivity to the formation of a protective film. Though most proponents of this theory believe the protective film is an oxide layer, others have presented experimental evidence which indicates that adsorbed gases (physically or chemi-adsorbed) also may promote passivation. Adsorbed films are thought to result in corrosion resistance by the satisfaction of surface secondary valence forces. The second theory, the Electron Configuration Theory, centers about the fact that most metals which exhibit passivity are those in the transition groups of the periodic table. The atoms of these elements (Cr, Ni, Fe, Mo, etc.) are characterized by incomplete inner shell (d electron) energy levels and by unfilled **d** energy bands in the metallic state. The state of passivity is ascribed to the condition of unfilled **d** bands in the metal or alloy, and the active state to the situation that in effect fills the **d** band with electrons. Thus, adsorbed oxygen or adsorbed oxidizing substances accompany maximum passivity because they are electron adsorbers and do not supply electrons to the metal surface atoms.

The passivity of alloys (e.g. Fe-Cr stainless steels) is attributed to an electron sharing mechanism between the atoms (e.g. iron and chromium) in the lattice. The mechanism for the increased nobility of potential and the decreased reactivity of passive metals and alloys is considered to reside largely in the surface-metal atoms, although in alloys electron interaction (sharing) occurs throughout the metal. However, it is the electron configuration of the surface metal atoms that determines the degree of reaction with a corrosive environment.

Passivation may result from such reactions in accordance with the second definition of passivity stated above due to the formation of protective layers of reaction product. In some cases, adsorption may occur, rather than reaction, which may promote passivation by the mechanism previously discussed. Adsorption or compound formation (reaction) is a function of the ratio of the energies involved in the work function of the metal (a measure of the heat of evaporation of electrons from a metal surface) and the heat of sublimation of the metal. When the work function is small and the ratio of work function to the heat of sublimation is equal to or less than one, adsorption and passivity will occur. When the energy necessary to dislodge an atom from the lattice is small and the ratio of work function to heat of sublimation is greater than one, then reaction will occur. Metals passive by the consideration of the Electron Configuration Theory may be considered to be covered with a monoatomic or monomolecular film. Thicker films of oxides or other compounds are not included as part of the essential mechanism of passivity. In a broad sense, this theory may be considered as a generalized theory which includes the film theory as a specialized situation depending upon surface electronic configuration.

Recently, an unified mechanism of passivity and inhibition, based on the behavior of local elements in metal surfaces, has been developed.[2] This mechanism suggests that passivity may be achieved either by: a) reduction of the open circuit potential differences between the local anodes and cathodes, b) increased anodic polarization, c) increased cathodic polarization, or d) a combination of these factors.

Under an Office of Naval Research contract, Professor H. H. Uhlig of the Massachusetts Institute of Technology, a leading proponent of the Electron Configuration Theory, is studying the "Effect of Electron Sharing and Intermetallic Compound Formation on the Corrosion of Metals." The purpose of

this project is to study the fundamental factors relative to electron-sharing and compound formation in several of the binary and ternary alloys in order to initiate a science of alloying with respect to the chemical properties of metal systems. The study will extend the Electron Configuration Theory of passivity and perform critical experiments designed to test its validity. Two phases of electron sharing have been initiated, namely the investigation of the chemical and physical properties of intermetallic compounds of magnesium (with Group IV B elements) and the study of the chemical properties of adsorbed metal films.

Studies recently have been completed on the compounds Mg_2Sn and Mg_2Sb. Some recent publications[3, 4] report on the measurement of electrical conductivity and thermoelectric power of magnesium-tin and magnesium-lead alloys, together with the compounds Mg_2Sn and Mg_2Pb, as functions of temperature and composition; and the quantitative evaluation and comparison of chemical properties of the alloys and compounds, including the measurement of solution potentials, rates of oxidation at high and low temperatures, rates of reaction in electrolytes, and reaction mechanisms.

It has been shown that Mg_2Sn is an electronic semi-conductor, i.e., the conductivity increases as an exponential function of temperature, whereas the temperature dependence of resistivity of Mg_2Pb is that of a normal metal. Both compounds are more reactive than magnesium when subjected to high temperature oxidation (350°-500°C). The solution potential measurements show that the potential is strongly dependent on the electrolyte. The corrosion reaction, in the absence of air, may be summarized as follows:

$$Mg_2Sn + 4H_2O = 2Mg(OH)_2 + Sn + H_2O$$

In pure water, single crystals of Mg_2Sn break down into geometric fragments. The rate of breakdown is a function of the hydroxyl ion concentration and occurs in the absence of stress.

The research on the study of Mg-Sn and Mg-Pb compounds is being extended to include Mg-Si and Mg-Ge so that the type of intermetallic bonding may be correlated with chemical and physical properties, especially passivity.

The promotion of passivity by adsorbed metal films is being studied initially with the iron-chromium system. Thin films of iron are deposited on chromium by evaporation and the iron film is then exposed to reagents, such as nitric acid. The residual iron made passive by electron interaction with the underlying chromium is detected either by chemical analysis or by use of radioactive isotopes. Precise determination of the thickness of the residual iron passivated by contact with the chromium will be made. The study later will be extended using evaporated films of copper and zinc. It is hoped that such work will give a clear insight into the mechanism of passivity in the stainless and related alloys. Research on the chemical behavior of metal films formed in vacuum and the effect of adsorbed substances, such as gases, on the corrosion characteristics of these films also is underway.

As part of the study of the nature of passivity in the stainless steels, the influence of surface treatment on the variation of potential of 18-8 with time is under investigation. It is believed that interstitial hydrogen may be a factor promoting this time-dependence behavior of the observed potential, and the effect of absorbed hydrogen on the changing potential will be evaluated.

The passivity of stainless steels also is being studied by Professor M. G. Fontana, of Ohio State University as part of his ONR program, "Fundamental Studies of Corrosion." The major objective of this research program is the study of the formation, breakdown and nature of surface films formed during the corrosion of metals at normal and elevated temperatures.

The results of these studies, thus far, indicate that 18-8S stainless steel can become passive by means of a physically adsorbed gas.[5, 6] At room temperatures, specimens of this alloy display passivity upon exposure to air and lose passivity upon exposure to reduced pressure (vacuum). This process is reversible in that the alloy can be passivated, broken down, repassivated, broken down and so on, by alternate exposure to air and vacuum. The ready breakdown of the passivity under vacuum at room temperature indicates physical adsorption. Oxides or chemisorbed gases would be considerably harder to remove or break down and would probably require elevated temperatures. Electron-diffraction studies also reveal no oxide films present on the surface. A diffuse and unidentified pattern was obtained which may be a hydrous oxide of nickel or chromium. This material may be of assistance in providing a surface that readily absorbs gases. It was found that the most effective passivation treatment of all those investigated was exposure to boiling sulfuric acid followed by exposure to air. Air passivation is regarded by Dr. Fontana as the true passivation of stainless steels. Vacuum breakdown of the passive films is pressure and time sensitive. The time for breakdown increases as the pressure increases, and there may be a critical pressure above which the films would not break down. Electron diffraction studies of sulfuric acid-air formed films show no changes taking place in the film as a result of prolonged air exposure.

Interestingly enough, the 18-8 stainless steel also was passivated by exposure to nitrogen, helium gas containing 1.5% nitrogen, and argon. Conclusive demonstration of these effects would provide strong support for this new theory involving a physically adsorbed gas. Gas adsorption studies on metal filings are underway to determine which gases and how much gas can be adsorbed at room temperature.

The passive film formed in boiling, distilled water does not break down under reduced pressure. It was also found that cold worked stainless steels cannot be passivated by the above methods.

Film stripping studies and electrolytic passivation studies have been initiated to study the structure of the films and potential breakdown measurements and

erosion-corrosion tests are being used to follow the breakdown of the passive films. Recent work has indicated that potential-time studies recording the characteristics of the specimen while undergoing an actual corrosion test are more informative and applicable to the study of passivation than potential breakdown measurements. Potential-time studies of active and passivated 18-8S stainless steel produced four general types of curves. One represented the active state while the others indicated three degres of passivity: adsorbed films of a physical and chemical nature and an oxide film.

A third aspect of passivity of metals is under investigation by Dr. N. Hackerman of the University of Texas as one phase of his research program on "Exchange Adsorption."

The passivity of chromium has been studied[7] by treating electrolytically deposited chromium surfaces with nitric acid and subsequently oxidizing them in air at various temperatures. Electron diffraction observations were correlated with electrode potential measurements. The conclusions reached were that an oxide film was not the primary cause of the passivity of chromium unless a thickness of the order of a monolayer is considered as a true oxide. It was shown, however, that oxide films can alter appreciably the values of the measured electrode potentials of the metal surface, although these noble potentials obtained with oxide films need not be identified with passivity. It appears that the rate of decay of the noble potential can be used in considering the "degree of passivity." Thus the potential changes rapidly to a more basic value for the less truly passive metal.

No evidence was obtained to indicate that an "oxide film" of monomolecular dimensions could not explain the behavior of the metal. The Electron Configuration Theory also explains the behavior of chromium satisfactorily, since this theory can be shown to account for the existence of a monolayer.

Dr. Hackerman also is studying the effect of chloride ions on passive metals. The extent and rate of association, or attachment, of chloride ions from aqueous solution on chromium and on stainless steel surfaces is being investigated by the use of radioactive chloride ion. It is well known that passive metals become active toward corrosion in the presence of halide (particularly chloride) ions but the actual mechanism of chloride induced corrosion still is not understood. It had been postulated that chloride ion catalyzes the breakdown of the electronic configuration of the surface metal atoms at certain local areas causing galvanic action to occur. Results of this study, thus far, suggest the possibilities of a chemisorbed layer of chloride ions, and indicate the importance of the chloride ion attachment as a factor in the destruction of passivity of chromium. The visible corrosion of the stainless steel samples increased with the amount of chloride ion on the surface as measured by "counting" techniques, and most extensive corrosion was observed in the most concentrated radioactive areas. Further work on this phase of the program is continuing.

The adsorption of gases on low carbon steel, stainless steel and chromium also is being studied to extend the existing knowledge concerning passivity by increasing both the number of metals and gases investigated. Isotherms of oxygen and chlorine adsorbed on 1020 steel, stainless steel and chromium powder have been obtained, and those of carbon monoxide and the oxides of nitrogen currently are being determined. Isotherms were obtained on the powders after either baking, reducing with tank hydrogen, or reducing with deoxygenated hydrogen. The results, thus far, show general trends of increased adsorption in the order of chromium, stainless steel, 1020 steel and baked, plain hydrogen reduced and deoxygenated-hydrogen reduced surfaces. In the case of chlorine, indications are strong that chemisorption occurs.

Experiments are underway to determine the exchange adsorption of chlorine gas on an oxygenated (passivated) chromium surface. Thus, the extent to which chlorine can replace oxygen and break the passive film will be determined.

Inhibitors and Passivators

The importance of inhibitors in preventing corrosion of metals is demonstrated by the widespread applications in metal cleaning, metal finishing and metal protection processes. It is agreed generally that corrosion inhibition by organic molecules is the result of the inhibitor molecule forming an adsorbed film over the metal which prevents penetration by corrosive agents and, therefore, causes the surface to be less susceptible to corrosive attack. However, the mechanism of the adsorption process, the effect of inhibitor molecule size and composition, and conditions surrounding the adsorbed layer in corrosive media are still unknown to a large extent. These factors are being studied by Dr. Hackerman, under the above contract, in a two-phase program of inhibitor action. The investigation of "The Adsorption of Polar Organic Compounds on Steel Surfaces" is concerned with adsorption of polar organic molecules (organic acids, alcohols, esters and amines) from a non-polar solvent, benzene, on metal surfaces which are relatively planar. Much of the past experimental work has been done on porous, high surface area solids. A method of measuring relatively small amounts of adsorption on planar surfaces has been developed and preliminary studies have been completed. A test to determine the effectiveness of various compounds as inhibitors has been devised and is being applied to all compounds studied.

Another phase of this program is the "Study of Adsorption of Inhibitors from Solution" by means of an EMF method. Dr. Hackerman has postulated that adsorption of corrosion inhibitors takes place over the entire surface of metals, thus reducing the galvanic corrosion due to local anode and cathode areas.[8,9] The adsorption of positive cationic inhibitor materials (e.g., amines) results in equipotentialization of the surface by causing a displacement of electrons from the metal (anodic area) toward the positively charged particle rather than toward the

cathodic area and provide a diffusion or resistance barrier. To demonstrate this, time-potential curves at various inhibitor concentrations on anodically and cathodically polarized specimens as well as on unpolarized specimens were obtained. A study of the adsorption of amine inhibitors on copper and steel specimens indicated that adsorption at anodic spots actually may cause a decrease in solution tendency, whereas adsorption at cathodic regions probably inhibits by means of diffusion, resistance changes or overvoltage effects. Continued investigation of the "partial oxidation" theory is underway to further the elucidation of the nature of the adsorption processes on metals from solutions.

The mechanism of inhibitor action afforded by the "passivator" group of compounds is being studied by Dr. Uhlig as part of his passivity research program. According to Uhlig[10] passivators usually are oxidizing agents which produce their effects by changing the potential of the base metal in a noble direction instead of producing merely a physical barrier to corrosion. The corrosion protection offered by chromates, hexametaphosphates, nitrites and other passivators is being investigated to gain a further insight into the true nature of passivator action. Corrosion rate studies, potential measurements and surveys making use of radioactive isotopes are being employed.

The investigation of the "Role of Inhibitor Films in Electrode Processes" was conducted by Dr. H. J. McDonald of the Illinois Institute of Technology. The chief objectives of this program were: a) to obtain polarization data on a number of representative metals, using anodic and cathodic inhibitors and, from the curves, determine if a scale of inhibitor effectiveness could be formulated; and b) to study the polarization characteristics of corrosion accelerators and contrast their behavior with that of corrosion inhibitors.

Two instruments, the Pulse Polarizer and Scope Polarizer, were developed for the quantitative evaluation of inhibitors by determining their effect on the electrode polarization of metals. The Pulse Polarizer employs a system of electronic circuits to polarize an electrode over a brief time interval. The polarization and depolarization at the surface of the electrode are recorded continuously on a high-speed strip chart and show up as a curve which is distinctive for each set of conditions. The polarizing circuit consisted of a condenser (125 mfd) which is charged to 310 volts. Discharge of this condenser brings about the polarization at the electrode surface. The polarization potential is amplied by means of an electronic DC voltage amplifier and then recorded.

Both anodic and cathodic polarization may be studied with the apparatus, but for inhibitor studies, cathodic polarization is of particular interest. The voltage applied is constant for each pulse, and the time interval during which the surface is polarized is between 0.05 and 0.1 sec. When a pulse is applied, the potential first drops to a new value corresponding to the polarization under extremely high current density, then the curves return toward the normal potential at various rates. A test usually is complete within several minutes. More detailed descriptions of the Pulse Polarizer and the results of the studies of a large variety of inhibitors have been reported.[11,12,13,14] It was found that the Pulse Polarizer is useful in establishing a relative scale of inhibitor effectiveness, but that complete interpretation of the polarization curves often was difficult.

In view of the difficulty of theoretical interpretation of the polarization curves, a study was undertaken on the "Influence of Surface Films on the Electrodeposition of Hydrogen on Palladium" in order to obtain a clearer understanding of the factors governing polarization phenomena and inhibitor effectiveness. It was found that the transmission of hydrogen through a palladium cathode depended largely upon the nature of the adsorbed surface film. Metallic films severely reduced the transmission of hydrogen, whereas adsorbed organic films might also cause an increase in the transmission depending upon the adsorption behavior of the compound and film thickness.

Galvanic Corrosion

As previously mentioned, galvanic corrosion is responsible for many major corrosion problems and generally is caused by dissimilar metal contacts or concentration cell effects. The subject of bimetallic corrosion has received considerable attention in the past, but it is still difficult to predict accurately the result of placing two metals in contact under a particular set of environmental conditions. The importance of environment often has been overlooked, and little is known yet concerning the kinetics of the cathode reaction which is a corrosion-controlling process. In order to gain more insight into the complicated phenomena which occur during bimetallic corrosion, Dr. R. T. Koenig, of the University of Colorado studied "Bimetallic Corrosion in Neutral Electrolytes" under Office of Navel Research contract. Two important factors influencing the amout and distribution of corrosion in bimetallic couples in neutral electrolytes were investigated:

1. the relative areas of anodic and cathodic metal; and
2. the varying composition and concentration of salt solutions.

Partial and total immersion tests with numerous metallic couples using different concentrations of sodium chloride and calcium chloride solutions are underway. These tests are bing supplemented by electrochemical studies of the oxygen depolarization reaction occuring at the various metal surfaces. Simple specimen shapes, utilizing coupling by means of threaded connections or by ring-plug combinations, are being employed. The specimens are free from local strains and avoid the high electrical resistance generally encountered when external electrical connections are used for coupling. Anodes of zinc and iron have been coupled with copper, brass, stainless steel and other metals, and many data have been accumulated. It appears, thus far, that the observations made differ markedly from those that have been reported previously in the literature. For example, it was found that under conditions where hydrogen evo-

lution is of minor importance in determining the corrosion rate, there is no noticeable effect of the actual junction of two metals upon the distribution or intensity of the resulting corrosion. A report summarizing the results of the investigation will be available in the near future.

The investigation and explanation of the phenomena occurring when a metal is placed in electrolyte, containing no ions of the exposed metal, is the objective of the research program at Clark University, under the direction of Dr. D. MacGillavry, Jr. Little systematic research on this general problem, the nature and behavior of metal-solution phase-boundary pontentials when no common ion is present, has been conducted and no adequate theory to explain the phenomena exists. These are extremely important in the corrosion of metals under practical conditions.

The research is in its early stages and it is planned, first, to develop techniques for the measurement of phase-boundary potentials; second, to determine how these potentials depend on a number of experimental factors, especially temperature, composition of the liquid phase, and composition of the electrode in case the metal is an alloy; and third, to use the experimental data as the basis for the theoretical explanation of the phenomena.

General Corrosion Studies

At the University of Oregon, Dr. P. Van Rysselberghe is studying corrosion phenomena using polarographic techniques. The polarographic method, invented about 1925 by Jaroslav Heyrosky, is based on the interpretation of the current-voltage curves that are obtained when solutions of electroreducible or electrooxidizable substances are electrolyzed in a cell in which one electrode consists of mercury falling dropwise from a very fine bore capillary glass tube.[15] From the unique characteristics of such current-voltage curves both the species and concentration of the electroreducible or electrooxidizable substances present in the solution can be determined. This sensitivity of the polarograph to minute concentration charges of reducible substances provides the basis of rapid and sensitive corrosion tests by following the consumption of oxygen, carbon dioxide, etc., by metallic surfaces dipped in electrolytic solutions containing these agents.

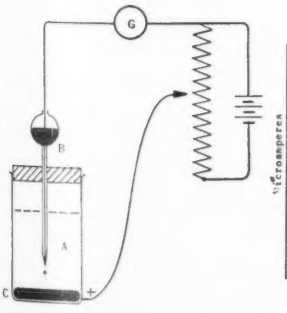

Figure 11—Schematic drawing of polarograph.

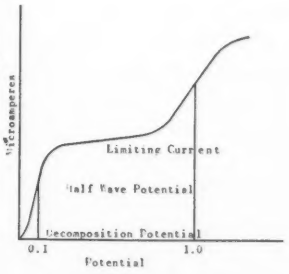

Figure 12—Oxygen polarogram.

In Figure 11 is shown a schematic arrangement for measuring current-voltage curves by the dropping mercury electrode, the polarograph. In this diagram, **A** is the electrolysis cell containing the solution to be analyzed, **B** is the dropping mercury, and **C** is a stationary pool of mercury on the bottom of the cell which serves as the second electrode. The dropping electrode consists of a drawn out capillary tube (whose internal diameter at the tip is about 0.03 mm) connected to a reservior of mercury. Mercury drops issue from the capillary at the rate of about one drop every 2 to 4 seconds. The drops are very small, having a maximum diameter at the breaking point of about only 0.5 mm. The cell is connected in series with a calibrated galvanometer, G, to a battery and rheostat, by means of which an electromotive force of the battery can be applied to the cell. The current-voltage curves are obtained by gradually increasing the applied electromotive force and noting the current indicated by the galvanometer. The current ordinarily is quite small, seldom exceeding 50 microamperes. A typical current-voltage curve, or polarogram of oxygen is shown in Figure 12. The potential at which the curve begins to show a rapid increase of current with a small increase in voltage is called the decomposition potential. The mid-point of the vertical portion is called the half-wave potential and the horizontal portion is the limiting current. The decomposition potential is characteristic of the substance and the height of the curve is a measure of its concentration. The first current break is caused by the reduction of oxygen to hydrogen peroxide and the second, by the reduction of the hydrogen peroxide.

It was established that percarbonates can form during the reduction of oxygen in the presence of carbon dioxide,[16] and on the basis of these studies the investigation of the consumption of oxygen, carbon dioxide and their mixtures by various metals and alloys was undertaken. The technique was to expose the metal in a salt solution containing known amounts of carbon dioxide or oxygen or both and by the use of the polarograph to determine the rate of disappearance of these gases. Polarograms of these tests indicated the importance of hydrogen peroxide formation during corrosion of zinc and aluminum and the influence of carbon dioxide in retarding the corrosion of these metals. Further research on the role of hydrogen peroxide and percarbonic acid in corrosion processes and on the application of polarographic techniques to the study of the rates of corrosion of metals currently is underway.

The "Fundamental Studies of Corrosion" program at Ohio State, in addition to the passivity studies discussed previously and the high temperature film studies to be described later, also encompasses studies on the intergranular corrosion of stainless steels, including the effects of stabilizing and welding treatments, and studies on the corrosion of copper and copper base alloys. The latter study will investigate the influence of velocity, oxygen concentration, temperature and time on the corrosion and "passivation" of copper and copper base alloys in various media. As an initial step, the influence of these factors on

the single electrode potential of copper in dilute sulfuric acid is being studied to determine the role of the copper ion and the oxygen concentration cell in the corrosion of copper. Future research subjects include the application of radioactive tracers in fundamental corrosion studies; investigation of the corrosion of titanium and its alloys; thermogalvanic corrosion; mechanism of internal oxidation and others.

At the University of Utah, Dr. George Hill is studying the "Corrosion of Metals in Contact with Liquids" in the light of the theory that the role of various gases and salts dissolved in water is largely that of providing ions for the conduction of electric current. The validity of this theory and the deternation of the specific effects of particular substances are being investigated by studying the influence of varying concentrations of SO_2, Cl_2, H_2S, CO_2, K_2CrO_4 etc. on the rate of corrosion of pure metals and alloys. The data will be interpreted in terms of Eyring's "Theory of Absolute Reaction Rates" which will give the free energy, heat and entropy of activation of the rate determining step, and an elucidation of the mechanism of the reactions.

High-Temperature Oxidation

The corrosion and oxidation of metals and alloys at elevated temperatures are rapidly becoming problems of major importance to the Navy. The performance of rockets, jet engines, guided missiles, etc. is dependent primarily upon the development of oxidation-resistant materials capable of withstanding extremely high temperatures and the erosive effects of hot gases. In this field also, the Office of Naval Research is supplementing other alloy development programs with several fundamental research programs aimed at the better understanding of the mechanisms and kinetics of high temperature oxidation processes.

Metals generally can be divided into two groups for consideration of their oxidation products. One group, composed of the lighter metals, forms porous oxides, which have a smaller volume than the equivalent metal consumed in producing these oxides. These metals generally exhibit a linear rate of oxidation at constant temperature. The second group, aluminum and the heavier metals, form protective, non-porous oxides of greater volume than the equivalent metal consumed. Many metals of this group exhibit a parabolic oxidation rate (inversely proportional to the square root of time). Under some conditions, the oxidation process is proportional to the logarithm of time.

Factors influencing the rate of oxidation and nature of the oxidation product are orientation of the base metal, lattice structure of the metallic substrate, metal composition, surface conditions and environment, and temperature. Although oxidation usually is considered a direct chemical reaction in which the rate is controlled by simple diffusion of the reacting atoms through a non-porous corrosion product film, recent work has demonstrated conclusively that oxidation may occur by metal ions diffusing outward through the film. This electrolytic theory of oxidation compares the growing film to a current-producing cell in which the metal-film interface acts as the anode supplying cations and electrons for outward diffusion and the environment-film interface acts as a cathode supplying the anions for inward diffusion. The film acts as both the internal and external circuit of a closed cell.

At the Illinois Institute of Technology, Dr. D. D. Cubicciotti is studying the "Determination of the Kinetics of Reactions of Metals with Gases at High Temperatures." The direct measurement of the rates of gas-metal reactions is being made by means of a gas volumetric method with gas circulation under atmospheric or low pressure. Microbalance techniques are being employed as an auxiliary method for equilibrium measurements and thin sheet investigations.

One of the initial phases of this program (which formerly was under the direction of Dr. H. J. McDonald) was the study of electropotentials in growing halide and oxide layers on metal.[17] An electrode probe was developed which enabled the experimental determinations of these electropotentials and the subsequent calculation of the ionic transference numbers. The probe method proved to be a sensitive tool, responding to all factors which influenced the transference numbers. The oxides on iron, stainless steel, nickel, aluminum, zinc, molybdenum and tungsten were found to be predominently electronic (cationic) conductors. In anionically conducting scale, where the zone of growth was at the scale-metal interface, previous criteria were found to be inadequate.

A study of the zone of metal phase consumption (locus between the initial surface of the metal and the surface of the retreating metal phase) revealed that even in the cases when a scale grows by outward diffusion of metal or metal ions, the scale also must grow on the other side towards the metal.[18] The conditions of scale growth on both sides of the scale are dissimilar; consequently, the structure of the scale tends to be different in both layers formed. A process of cavity and column formation and exchange of oxygen in the zone of metal phase consumption was postulated. It also was noted that as a consequence of secondary processes, diassociation and recrystallization may be responsible for a third layer formation.

Current work under way includes the study of the effects of ionization of gases on oxidation rates at high temperatures and the determination of the rates of reactions of zirconium and beryllium with oxygen, nitrogen and oxides of nitrogen.

As previously indicated, one phase of the "Fundamental Corrosion Research" program at Ohio State University is concerned with the nature and protective value of surface films formed on metals and alloys at high temperatures. The composition and structure of these films are being investigated by chemical and metallographic examination and by electron-diffraction studies. The mechanism and rate of formation, limiting temperatures and other pertinent factors are being investigated. Such information is useful for prediction of the service life of alloys

operating at high temperatures and is valuable for the scientific development of improved alloys.

Several of the stainless steel varieties have been exposed to varying oxygen atmospheres for different temperatures and time treatments, and the oxidation process followed by weight measurements and diffraction studies. Although considerable data have been accumulated, the analysis has not reached the point where definite conclusions have been drawn. Over short periods of time, for a number of the steels, oxidation proceeds in accordance with a logarithmic rate, changing to the parabolic relationship with longer exposure time periods. One interesting observation of some preliminary studies of 18-8S at 1800° F. was that oxide films formed in low-oxygen atmospheres are more protective to further oxidation than scales formed in higher-oxygen atmospheres. This indicates the possibility of developing pre-induced films by pre-treatment for increased oxidation resistance.

Somewhat similar studies are being conducted by Prof. H. J. Yearian at Purdue University under Project SQUID. The objective of this program is the study of corrosion in connection with jet propulsion. The purpose of the research is to identify the corrosion products and to investigate the process of corrosion and its dependence on the chemical and physical properties of the materials and on the conditions of exposure. The formation, structure, properties, and resistive function of oxides, formed in high temperatures, and gaseous oxidation of ferrous alloys (in air and oxygen atmospheres) are being investigated.

Electron diffraction techniques are being used to study thin oxide films and the surface of thicker oxide layers. The diffraction patterns are obtained at temperatures of oxidation by means of special instrumentation. The physical arrangements of the oxides in the scale layers will be studied by optical microscopy, X-ray-microradiography and photoelectric image formation methods. Electron microscopy will be used to study oxide formation relative to grain boundary precipitation of carbides and/or nitrides in high chrome steels.

The high temperature oxidation products formed in oxygen and in air on chromium steels, ranging from 5 to 26 percent chromium content, have been analyzed by X-ray diffraction. A regular variation of phases present can be correlated with change in oxidation resistance. In contrast with pure iron, no FeO was found in the oxidation of iron-chromium alloys, indicating a possible function of chromium in producing an oxidation resistant material. The resistance to oxidation generally decreases as the chromium content of the alloy is diminished and as the temperature is increased. A limited amount of work on the air oxidation of nickel-chromium steel also has been completed.

These oxide "existence" studies in oxygen atmospheres at various temperatures and times, using X-ray analyses of the bulk oxides, are continuing to determine more definitely the correlation between oxide structure and oxidation resistance.

Since it is recognized that the protection afforded a metal by its oxide coating may not be due to the bulk oxide acting as a mechanical barrier separating the reactants, but rather to some special properties of a relatively thin layer, presumably next to the metal, a considerable portion of the research is being directed toward the investigation of the formation, structure and properties of thin oxide films, using electron diffraction and electron-microscope techniques. For the diffraction studies, oxidation is being accomplished *in situ* in the diffraction camera.

Film stripping techniques also are being utilized to examine thin films by transmission electron diffraction. The electrical properties of the protective oxide layers, as a function of composition and temperature also will be investigated.

The diffusion mechanisms operating during oxidation processes are being studied as part of a large comprehensive program at Carnegie Institute of Technology on the "Kinetics of Reaction in the Solid State" under the direction of Dr. R. F. Mehl. This program is making extensive use of radioactive tracers in the study of diffusion processes, since the techniques are extremely adaptable to the study of diffusion mechanisms in oxide films, thereby allowing the determination of the mechanisms of the scaling of metals. It is possible thus to determine whether it is iron or oxygen which diffuses through the oxide layer during the scaling of iron. A thin layer of radioactive iron is electroplated on a polished surface of pure iron and subsequently oxidized under controlled conditions. The distribution of radioactive iron through the scale indicates the nature of the diffusion process.

Initial results already have indicated that the generally accepted mechanism of oxidation of iron is not sufficiently adequate and it is hoped that information derived from these studies, together with kinetic data now available in the literature will permit a complete reconsideration of the mechanism and kinetics of the scaling of iron. Future work will include the oxidation of copper and other metals.

It is well known that most metals, including the common heat-resisting alloys suffer a progressive deterioration in strength and in ductility when they are stressed at high temperatures for a considerable length of time. Whether deterioration is due solely to the effects of time, temperature and stress or whether atmosphere reactions are an important cause of deterioration has not been investigated thoroughly in the past. There is some evidence in the literature that atmosphere reactions have an important effect on high temperature deterioration of metals. For instance it has been shown that, during stress-rupture tests of steels in oxidizing atmospheres, the slope of the rupture-time curve (which is a straight line on a log-log plot) changes abruptly after a finite test time. The change of slope occurs at the same time as intergranular oxidation occurs, and generally the fracture changes from a ductile transcrystalline failure to a brittle intergranular type. The same metal tested in an oxygen-free atmosphere does not exhibit these characteristics. The effect of atmosphere reactions on heat-resisting alloys, a potentially important prob-

lem in high temperature power plants, has been investigated only to a limited extent and the results are not conclusive.

In order to investigate these effects, Prof. O. C. Shepard at Stanford University is studying the "Effects of Atmosphere Reaction on the Deterioration of Metals at Elevated Temperatures." This program first will determine whether atmosphere reactions have an important effect on the stress-rupture properties of high-temperature alloys and then by the use of simple, pure metals determine the mechanism and nature of these effects. Tests are being conducted in inert atmospheres and various environmental atmospheres in which heat-resisting alloys commonly are used.

Results to date indicate atmosphere reactions have a definite effect upon the high-temperature strength properties of metals and alloys. Low-carbon steel specimens subjected to an inert, purified helium atmosphere, exhibited greater and more uniform ductility and greater rupture life than specimens tested in atmospheres containing hydrogen, water vapor, oxygen and air. The latter specimens exhibited brittle failure with numerous surface cracks. Confirmatory tests are underway. The program also will include the study of the effect of strain rate on the embrittlement of pure metals subjected to stress-rupture tests in active and inert atmospheres at elevated temperatures, in order to determine whether the reduction in ductility is due to the environment or the effect of low strain rates and high temperatures.

A discussion of the above presented corrosion research program would not be complete without consideration of the support provided not only by the closely allied fields of study within the Metallurgy and Chemistry Branches of the Office of Naval Research, but by many other rescarch projects under way throughout the other scientific divisions of ONR. Particular emphasis must be made of the interrelationship to corrosion of the research programs in such fields as electrochemistry, metallurgy, adsorption, surface reactions, diffusion and other solid state reactions. Much fundamental information will be forthcoming from these programs which will aid in the understanding and control of the numerous corrosion processes encountered in day-to-day operations. To cite a specific example of the cross-fertilization of research programs, it may have been noted that there were no projects in the current corrosion research program specifically directed towards the study of stress-corrosion cracking of metals and alloys. However, several metallurgical and chemical research projects now underway will make definite contributions to the understanding of the mechanisms of stress-corrosion cracking. Studies on diffusion, flow and fracture of metals, grain boundary behavior and numerous phases of the above corrosion projects are accumulating knowledge which will aid in interpreting the stress-corrosion behavior of metal systems. It might be said that as a start toward the problem, independent investigation is under way of the fundamental nature and laws of corrosion and the behavior of metals under a state of stress, which ultimately can be combined for the solution of stress-corrosion problems.

It must be borne in mind that this report does not include the large amount of corrosion work underway in the many laboratories of the material Bureaus and the Naval Research Laboratory. Space does not permit a description of the extensive efforts made by these activities to solve important specific naval corrosion problems.

In conclusion, the authors desire to point out that in their presentation of the corrosion research program of the Office of Naval Research, no attempt was made to present all significant findings of each project. Those readers who might be interested in details of a specific project are referred to the list of references appended to this paper. Future progress of the studies described above will be reported similarly by the project investigators in the usual scientific journals.

We hope the above summarization will provide an adequate picture of the research undertaken by the Office of Naval Research to further the understanding of why metals do or do not corrode and to study the mechanisms and kinetics of corrosion reactions so that predictions may be made of the behavior, towards corrosion, of metals and alloys under any environmental conditions likely to be encountered by the Navy. It often is pointed out that the Navy, despite the development of passivators, inhibitors, rust preventives, corrosion resistant alloys, protective coatings and whatnot still depends upon the old method of chipping hammer and paint brush for corrosion control. It is hoped that results of this and other similar programs will provide the necessary information to afford scientific control over the ubiquitous processes of corrosion and to insure unfailing corrosion protection.

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Special Anodes for the Cathodic Protection of Water Tanks ★

By A. L. KIMMEL

Introduction

THERE ARE in use today two electrical methods for corrosion prevention. The first consists of connecting a suitable metal to the structure to be protected so that a galvanic couple is set up, with the structure acting as the cathode of the system. The second is to place some inert electrode in or near the structure, and by means of an external source of direct current, cause the structure to act as the cathode of an electroplating system. Both methods will give good protection when properly applied and each has its own advantages. Experimental results have indicated that the two methods when properly combined can yield a corrosion prevention system of high efficiency and economy.

When iron or steel is protected galvanically by magnesium it is observed that after a period the cathode (iron, steel, etc.) becomes coated with a white deposit. Fergus[1] expresses his views concerning the protective value of these alkaline earth coatings in his publication on hot water heater protection. In the work on cathodic protection by O'Brien,[2] he reported that films of calcium hydroxide formed during his experiments on cathodic protection.

He further states that proper protection depends on maintaining these films. In his experiments the source of calcium was that present in the water. One such deposit was prepared in this laboratory and yielded the chemical analysis shown in Table I. Figure 1 shows this coating on the iron cathode before analysis.

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Assistant professor of chemical engineering at the University of Florida, is in charge of corrosion research for the Engineering and Industrial Station. He has devoted the past four years to water tank protection problems, fundamental studies of cathodic protection and general metal corrosion research. He holds degrees of B.Ch.E. and M.Ch.E. from University of Louisvilla, Ky., and was in charge of paint and varnish development for a Louisville paint company before coming to Florida.

A further indication that these coatings have protective values is the process of Cox.[3] He prepared his coatings by electrolizing sea water at various current densities using an inert anode and the metal to be protected (iron) as a cathode. The coatings then were rendered insoluble by a treatment of sodium silicate, the final coatings consist chiefly of magnesium and calcium silicates.

The work by Humble,[4] who used magnesium anodes in a galvanic system for protecting steel in sea water, reported the formation of these alkaline earth films on the steel and that after their formation the cathode current density could be reduced. He further reported that these films formed because of the alkaline condition at the cathode surface produced by the current flow.

The coatings as prepared in fresh water supplies using magnesium anodes will protect iron or steel for a limited length of time even when the anode is removed. However, they are slightly soluble and the time of protection is dependent on the rate at which the magnesium hydroxide is dissolved by the water.

Work at this station has shown that cathodic protection installations (systems using inert anodes and external D.C. supply) will give better protection with cathode current densities lower than normally used if the walls of the water tank are coated with these alkaline earth hydroxides. Two satisfactory methods have been used to prepare oxide films. In the first method, a rod or bar of magnesium was suspended and connected to the anode assembly. In the second method an inert anode or anodes were coated with magnesium oxide and a suitable binder such as plas-

★ Voluntarily submitted for publication January 24, 1949.

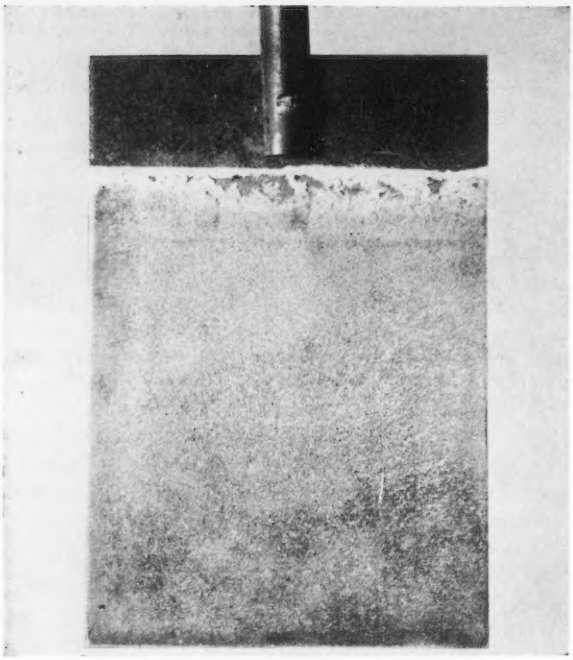

Figure 1

TABLE I
Typical Analysis of Coating Formed by Magnesium on Iron*

MgO	89.9%
CaO	7.8%
Remainder	2.3%

* Analysis based on ignited sample of prepared coating.

ter of paris or sodium silicate. Both methods produced good films in a relatively short period. Good results were obtained on both panels in the laboratory and in a 250-gallon water tank. It was further found, that once these films were formed, good protection was obtained even at very reduced cathode current densities.

Mechanism of Film Formation

In order to understand the method by which the alkaline earth hydroxide films form it is necessary to know something of their physical properties. In water solutions these compounds are in the hydrated state ($MgO-H_2O$ sometimes written as the hydroxide $Mg(OH)_2$). The solubility of this compound changes with the pH of the solution—the lower the pH the greater the solubility. Table II shows the solubility of magnesium hydroxide in solutions of varying pH values.[5]

When an electric current is passed through water, as in cathodic protection, there is a tendency for hydrogen ions to concentrate at the anode, and hydroxide ions at the cathode. The concentration of these ions is dependent on the current densities at the respective electrodes. These values can be measured and the curve Figure 2 shows these values at various anode and cathode current densities. The sketch Figure 3 shows the pH distribution between the electrodes in series of laboratory experiments using stainless steel electrodes and Gainesville, Florida city water as the electrolyte. It will be noted

TABLE II

Solution pH	Solubility of Mg++ ions moles per liter
pH = 9	1.2 x 10-1
pH = 10	1.2 x 10-3
pH = 11	1.2 x 11-5
pH = 12	1.2 x 10-7
pH = 13	1.2 x 10-9

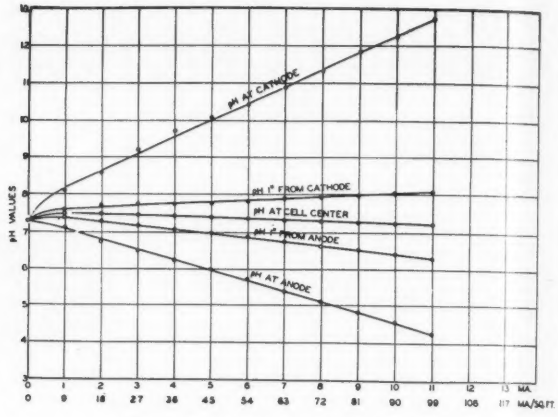

Figure 2—pH value vs. current density.

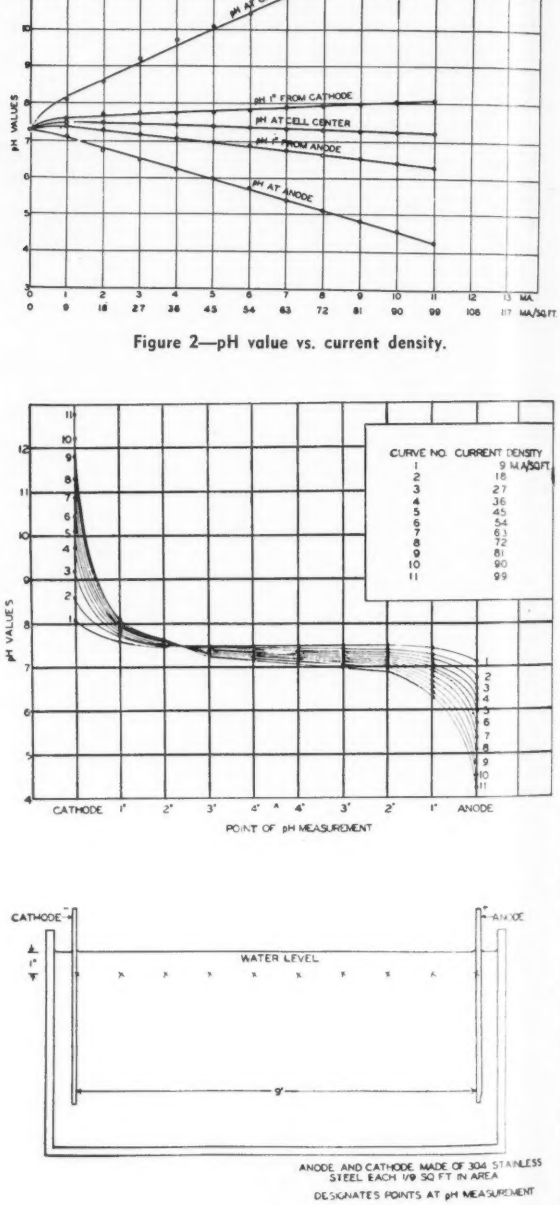

Figure 3—pH distribution across an electrolytic cell.

that at the surface of the cathode the concentration of hydroxyl ions [(OH)] is very high.

If in the arrangement shown in Figure 4 the anode were coated with magnesium metal or magnesium oxide the conditions are such that the magnesium hydroxide formed (chemically or electrically) is readily soluble and goes into solution forming magnesium ions. As these ions diffuse toward the cathode, they become less and less soluble and are precipitated out of solution. On reaching the cathode some of the remaining ions will deposit as magnesium hydroxide on its surface and slowly build up a continuous film.

When the source of magnesium ions on the anode has been used up the hydroxide ion concentration at the cathode surface is still the same, therefore, the film on its surface will require an extremely long time to dissolve. However, if the current is shut off, the water flowing through the cell will dissolve this protective film at a greater rate.

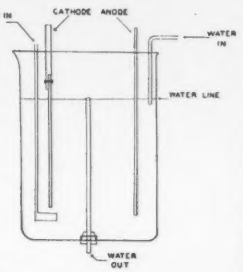

Figure 4—(Top) Cell arrangement.

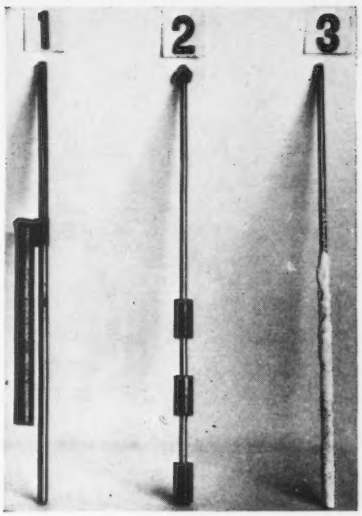

Figure 5—(Right) Electrode types.

Experimental Work

A number of cells were prepared as shown in Figure 4 and were arranged so it could be determined what effects rate of water change and aeration would have on the film formation and its protective value. These results then were evaluated and tried on a 250-gallon water tank. For laboratory work a four liter pyrex beaker was used as the electrolyte container.

Anodes used for the laboratory experiments were of three distinct types. See Figure 5.

1. 3/16″ stainless steel rod to which was connected a 5/16″ magnesium rod. (The magnesium rod was removed after an apparent cathode film was formed.)
2. 3/16″ stainless steel rod on which were press fitted 3-5/8″ diameter ½″ long magnesium metal cylinders.

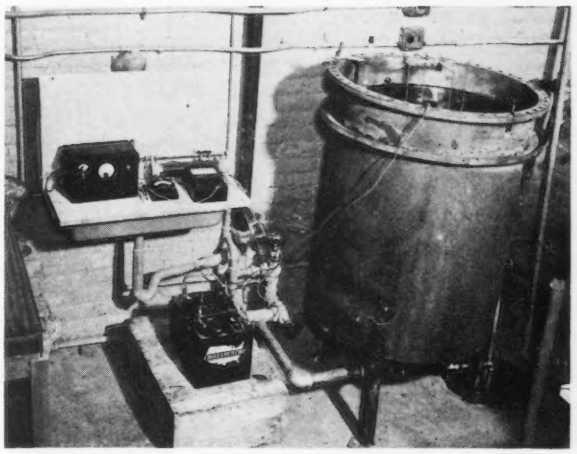

Figure 6—Small water tank used in experiments.

TABLE III

(Initial Current Density 3.6 Ma/sq. ft.)

CELL NO.	Type Anode	First Appearance of Cathode Film Hr.	Protective Current Ma/sq/ft. After Film Formed	Water Change Rate cc /day	Rate of Aeration cc/min.	First Sign of Corrosion (Days)	Film Forming Material at the Anode	Duration of Tests (Days)	REMARKS
1	1	..	....	4,000	..	None	....	90	Stainless steel anode—std. run.
2	1	36	1.0	4,000	..	65	Mg	90	Only small spots of rust appeared.
3	1	36	0.0	4,000	..	17	Mg	20	Large areas of the cathode showed rust.
4	1	36	1.0	12,000	..	28	Mg	40	Large areas of the cathode showed rust.
5	1	36	2.0	4,000	..	None	Mg	90	No sign of rust on cathode.
6	1	39	2.0	12,000	..	None	Mg	90	No sign of rust on cathode.
7	1	34	2.0	4,000	1	None	Mg	90	No sign of rust on cathode.
8	1	39	2.0	12,000	5	None	Mg	90	No sign of rust on cathode.
9	2	36	1.5	4,000	..	None	Mg	90	No sign of rust on cathode.
10	2	38	1.5	12,000	..	78	Mg	90	Only three small spots of rust.
11	2	44	2.0	12,000	..	None	Mg	90	No rust on cathode.
12	3	26	1.5	4,000	..	None	MgO^4	100	No rust on cathode.
13	3	None	..	4,000	..	....	MgO^5	5	No film formed—anode binder material unsatisfactory.
14	3	30	1.5	4,000	..	30	MgO^6	50	Anode coating flaked off before a good protective film formed.
15	3	32	1.5	12,000	..	88	MgO^4	90	Large number of rust spots on the cathode.
16	3	32	2	12,000	..	None	MgO^4	100	No rust spots appeared on cathode.
17	1[1]	72	2	30[3]	..	None	Mg	90	No rust spots appeared on cathode (See Fig. 7).
18	1[1]	72	2	30[3]	..	80	Mg	90	No rust spots appeared on cathode.
19	3[2]	72	2	30[3]	..	80	MgO^4	90	Small rust spots on cathode.[7]

1. Modified.
2. Four used.
3. Gallons per day.
4. Binder plaster of Paris.
5. Binder linseed oil.
6. In Na_2SiO_3.
7. Anode material flaked off rapidly during film forming process.

3. 3/16" stainless steel rods coated with magnesium oxide with the following binders:
   a. plaster of paris
   b. sodium silicate
   c. linseed oil

Anodes used in the small water tank were of similar construction.

Cathodes for the laboratory experiments were 4" by 6" plates of No. 16 gage hot rolled iron. The plates were prepared for use by sand blasting followed by pickling in dilute hydrochloric acid.

Conclusions

Results of this experimental work indicate anodes constructed to contain a source of Mg ions can be used effectively in fresh water systems to produce highly efficient cathodic protection systems. Good films of Mg $(OH)_2$ are formed rapidly on the cathode, and once formed efficient protection can be obtained at low current densities. Results further indicate (as did the work of O'Brien[2]) the role of the flowing current is not so much protection, but more film maintenance. Anodes of this type are feasable because once the oxide films are formed, there is no longer a need for a source of Mg ions.

The 250-gallon water tank was constructed of ¼" mild steel. It was prepared for use by wire brushing the surface to bare metal.

In all cases, Gainsville, Florida city tap water was used as the electrolyte. This water has a pH value of 7.2 and contains about 275 ppm dissolved solids. Of this 57 ppm are calcium and 16 ppm are magnesium. These are average values.

Experimental Procedure

The cathode coatings were formed at the current density necessary to protect iron under the conditions present. This value was obtained by a Britton curve[6] for this water assuming a drop in cathode potential of —0.2 volts would be sufficient. The value was then checked experimentally and in each case proved adequate. Once these films were formed the cathode current was decreased to lower values and observations were made over a period of three months to determine the extent of protection. In the laboratory cell systems the tests were studied while varying the water change rate, and some with variation in aeration rate, while in the small water tank only water change rate was considered. Since this information is to be useful only for water tanks the aeration rate was not considered a necessary factor. No effort was made in any case to determine the efficiency of the plating operations. The results of these experiments are shown in Table III with suitable remarks.

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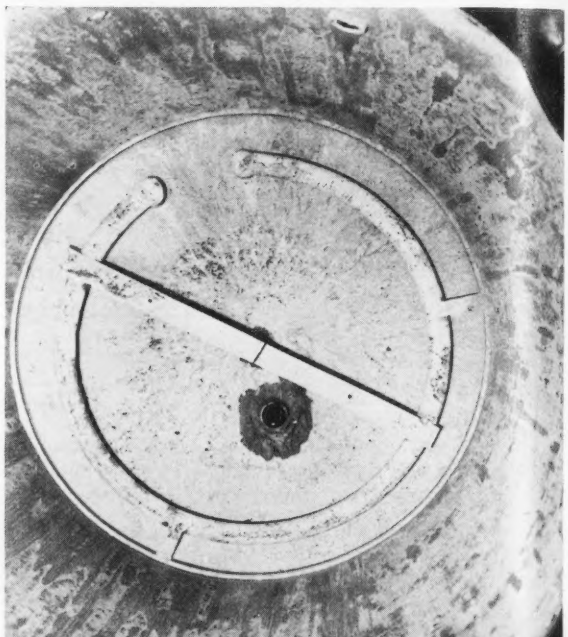

Figure 7—Interior of small water tank showing oxide film.

Modern travel type coating and wrapping machine showing pipe suspended by two traveling cradles. Enamel is fed to coating machine hopper through flexible metal conduit from the large-capacity mobile coating kettle.

Development of Pipe Line Coatings And Mechanical Application Methods*

By ***STEPHEN D. DAY***

IN ANY DISCUSSION of subsurface pipe protection it first is necessary that the high points in the history of the development of adequate pipe coatings and successful methods of applying them are understood so that a clear picture is presented.

Prior to 1925 very little study had been made by operating men and management of pipe line companies to determine the causes of corrosion and to establish working methods to mitigate them. It was, of course, known that underground metallic structures were subject to corrosion and that something should be done to protect these structures against partial or total failure. Very little research of a concerted nature had been done so that little was known of the basic causes of subsurface corrosion. With this condition existing it followed that pipe coatings and equipment to apply them to pipe surfaces were primiitve and largely unsuccessful up to that time.

Before 1925, the building of natural gas pipe lines was in its infancy. They had been built in California, Texas, Oklahoma, Arkansas, Ohio, Pennsylvania, and West Virginia but were limited to a distance of not over three hundred miles.

On the other hand, oil pipe lines had been successfully delivering oil in large volume long before natural gas was being moved through steel pipe in the middle twenties. Heavy wall steel pipe in short lengths connected by screw collars was "standard" with the oil companies at that time. Thousands of miles of pipe were in service in diameters not exceeding ten inches. Much of this pipe was coated and wrapped in primitive fashion using molten asphalt in combination with asphalt-impregnated asbestos felt, rag felt, and/or osnaburg wrapper.

With the development of high carbon steel pipe with thin walls and high tensile strength, the perfecting of the electric arc weld and more efficient pumping equipment, it was imperative that pipe coating and well-designed equipment to apply the coating to pipe surfaces keep step.

This problem was recognized by the American Gas Association which appointed Dr. Scott Ewing to explore the problem of adequate pipe protection through research and exhaustive testing under various soil conditions. The American Petroleum Institute did likewise and appointed Dr. Gordon Scott in 1930 to institute and conduct tests on both oil lines in service and nipples in all parts of the United States. This great test or series of tests had come to be known as the "three cornered test" since it was participated in by the oil companies, the coating manufacturers and the A.P.I.

Under Dr. Scott's direction these tests were started in 1930 and were to be inspected annually for five years. Inspections were made and results recorded in 1931 and 1932, but were passed over in 1933 when

* A paper presented at the Short Course on Gas Technology at Texas College of Arts and Industries, Kingsville, Texas, June 4, 1948.

data collected previously indicated a two-year interval might define the trend more clearly. The next inspection was made in 1934.

It was then decided to pass over the 1935 inspection and wait five years, or until 1940. This final inspection was made in that year under Dr. K. H. Logan of Washington, D. C.

Pipe Coatings in Use

While a large number of so-called pipe coatings appeared on the American market in 1928, they soon folded their tents and stole away when the findings of the first year inspection of the "three cornered test" were studied. All cold paints of bituminous base and fluidized with solvents of same derivation were found to be of little value.

It has been established that all bituminous type coatings whether produced from asphalts or from coal tar pitch should have the following basic requirements for an effective long lasting coating:

a. Continuity
b. Adhesion to pipe surface
c. Resistance to deformation under pressure
d. Resistance to moisture absorption
e. Resistance to cracking and softening under anticipated temperature conditions
f. Low electrical conductance.
g. Chemically inert under subsoil conditions.

Emerging from these "three cornered tests" were four types of coatings, each of which gave promise of providing adequate subsoil pipe protection when properly applied.

These four were: 1. Coal tar enamel; 2. Asphalt; 3. Petroleum compounds or greases, and 4. Bituminous mastics.

These basic types will be described in the same order.

Coal Tar Enamels

Coal Tar Primers

Considering materials separately from construction or application, primers and their function may be considered first. Primers are applied to provide bond of the completed coating to the steel.

Primers consist of pitch bases mixed with solvents recovered when the tars are distilled. When the primer has dried by partial evaporation of its solvents the film on the pipe is in reality a thin deposit of coal-tar pitch of the same nature as the enamel which will be applied over the primer.

The softening point of the primer deposit on the pipe, or in other words the softening point of the primer residue after evaporation of its solvents is approximately 150 to 170 degrees F. It is this characteristic which induces the important factor of bond.

The application temperature of enamels ranges between 350 to 475 degrees F and these temperatures are approximately 200 to 300 degrees F higher than the softening point of the primer. When the hot enamel is applied the primer is instantly softened or melted and the primer and enamel fuse together and bond is secured.

STEPHEN D. DAY

Has been identified with the pipe line industry for more than 20 years, concentrating his efforts largely on coatings designed to mitigate underground corrosion. He has made an intensive study of industrial corrosion problems. He was born in Orange, N. J., and served in World War I in the field artillery and air corps. He presently heads his own manufacturers' representative company in Houston.

The latest developments in primers consists of producing them with neutral or "sweet" solvents mixed with the pitch bases in proportions to provide a viscosity enabling the priming material to be applied in the thickness required to produce optimum bond. Low viscosity primers in the past have provided coats so thin that there was insufficient volume to produce bond, and high viscosity materials have left thick heavy coats drying to a gummy consistency with resultant poor bond or the formation of blisters or bubbles in the enamel coating because the heat of the enamel causes the solvents remaining in the primer film to gassify.

Later developments in primers consist of materials which will dry rapidly in winter so that coating work may progress along with other phases of construction during cold weather.

This development in primers as a cold weather material, is important when it is remembered that in former years pipelining was brought practically to a standstill in northern sections of the country during cold weather months because of slow drying and the inability of operators to keep coating progress up to the speed of other operations.

It is true that the best of the present day primers may be applied in coats either too heavy or too thin to provide the base for the best bond of enamel. This danger, however, has been eliminated in large measure as a result of the development of cleaning and priming machines with which the flow may be regulated closely.

Primers originally were applied by what was known as the "flip-flop" or the "criss-cross" methods before mechanical application was developed. In the flip-flop method, primer was poured over the pipe from cans and a workman pulled the saturated rug up and flipped it onto the pipe while a workman on the opposite side of the pipe pulled the rug back and flipped it over the top of the pipe on his side. The criss-cross method consisted of wrapping a rag around the pipe with one turn, saturating it with primer and workmen on each side would pull the rag back and forth. Naturally the more primer flooded on the rags or rugs the easier they would slip around the pipe, so it was common to see primer "curtains" or festoons hanging below the pipe.

The mechanical application of primers both in central application points and at yards and in the field over the ditch has been responsible largely for improvement of present day quality of most applications.

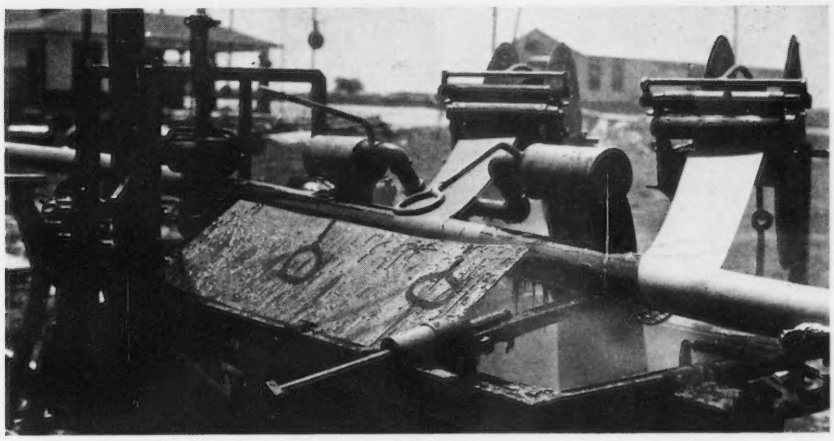

Figure 1—A close-up of the stationary Carroll Coating and Wrapping Machine. This was developed in the early thirties and did a good job of coating and wrapping small diameter pipe. Picture was taken in Lake Charles, La.

Coal Tar Pipe Coating, or Enamel

Coal tar "enamel" as the pipe line industry terms it, is produced from carefully selected coal tar pitch of a definite melting point established to close tolerances. To this is added fine ground filler consisting of mica, slate flour, or other minerals depending on the manufacturer. The amount of filler percentage-wise, depending on whose product it is, ranges from a low of 15 percent to a high of 35 percent.

It should be mentioned here that coal tar enamel manufacturers also make what is known in the industry as plasticized pitch-base enamels. These enamels were made first to protect steel water lines and proved of great value when used as inner linings in water mains.

The preparation of coal tar for application to the pipe is as follows: The enamel is chopped up in lumps weighing about fifty pounds which are placed in a mobile tar pot or kettle and melted at temperatures ranging from 375 degrees F to 450 degrees F depending on the product. The enamel then is ready for application to the pipe.

When coal tar enamel first was used on long lines it was believed that it would not be necessary to shield it with felts or wrappers. However, it failed to meet requirements a, c, and e, which caused requirement f also to fall by the wayside.

Continuity of coating was impossible when only one application of enamel was used. Then too, application methods were crude because at that time efficient equipment which would produce a continuous coating had not been developed.

Briefly, whether the pipe was all welded or was coupled the method of application was as follows:

From about 1928 to 1935 a high percentage of pipe was mill primed with coal tar primer. How primer was applied manually in the field has been described. This followed the field cleaning operation. After the prime coat had dried, a hot coat of molten coal tar enamel was applied to the pipe using a sling application method which employed two men to hold the sling against the bottom of the pipe and one man to pour the enamel on top of the pipe, all three men moving along the pipe at a steady pace and pouring sufficient coating on the top round of pipe so that the overflow filled the sling, thus coating the bottom of the pipe. A variation of this method was used when the pipe was to be coupled instead of welded.

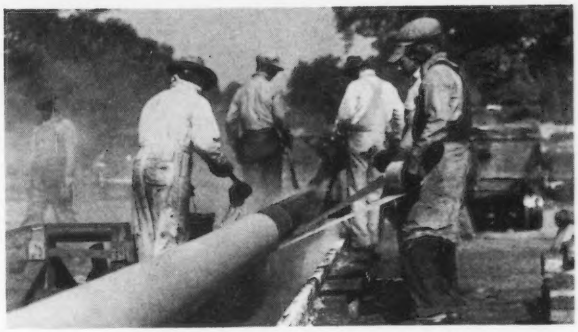

Figure 2—Stationary coating and wrapping operation. While pipe is rotated it is coated and wrapped by men working on a board platform. Picture was taken at Gulfport, Miss.

Figure 3—Creosoted cypress housing built to hold hot enamel over all portions of a patented coupling. These were used successfully on Lone Star Gas Company 20-inch line laid in 1935 with terminus at Irving Station, Texas.

In this case the pipe was turned on large roller bearing dollies and pipe was coated by a pouring man on one side of the pipe with another man on the opposite side facing him who used a metal spreader,

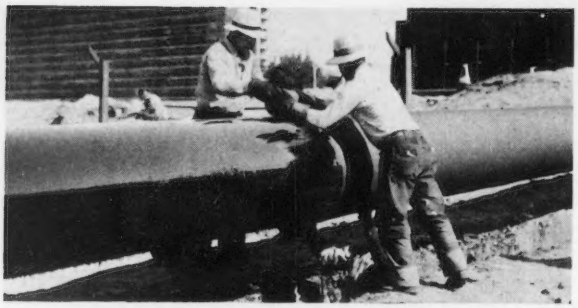

Figure 4—Hand-wrapping large diameter pipe at Bakersfield, California, in 1932.

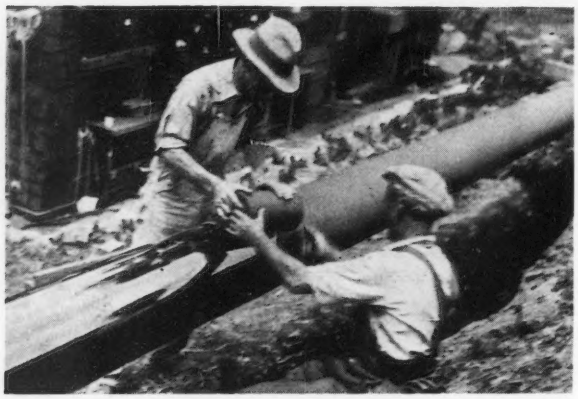

Figure 5—Hand-wrapping a 12-inch line in the winter of 1931-32 at Laguna Beach, Calif. The pipe was double coated by hand on this section using the sling method, then it was wrapped as a separate operation.

something like a plasterer's trowel, to spread and level off the molten enamel.

Resistance to deformation under pressure was never possible under subsoil temperatures and disparity of pressures encountered. As mentioned earlier, many tests conducted in all parts of the country had begun to piece together the true facts regarding service performance of coatings and there was no doubt that coal tar coatings required a shield or wrapper to equalize disparity of subsoil pressure and to prevent the coatings from moving toward the bottom of the pipe.

Resistance to cracking and softening under anticipated temperature conditions was unsatisfactory with an unshielded pipe line enamel coating. Frequently some time may elapse after the pipe is coated before it is laid and covered. If it is exposed to critical temperatures of heat and cold hair line cracks may appear below 35 degrees F and sliding may appear above 100 degrees F. It must be borne in mind that black surface temperatures run well above atmospheric readings, for example, pipe which has been primed with a black prime coat often shows temperature readings averaging 45 degrees F above atmospheric readings.

Asphalts

The comments noted above concerning coal tar coatings (or enamels) refer with greater force to hot coatings of asphalt base materials. At one time these coatings were used extensively by the oil industry as pipe coatings. One very practical reason for this use was that with the rapidly expanding production of gasoline and other finished products asphalt also was increasing because it was a by-product of petroleum refining. The oil pipe line companies used hot asphalt as pipe coating with or without shields or reinforcing felt and in single or multiple applications. Today asphalt base coatings are used less and less by the oil industry and hardly at all by the natural gas industry.

It might be well here to mention that during this period bituminous coatings were first shielded with asbestos felt spirally applied both manually and mechanically.

In 1930 the United Gas Pipe Line Company built a gas pipe line system from Kirbyville in Texas east to Franklin, Louisiana. The trunk line of this system used several types of protective coatings but the entire line was shielded with tar saturated asbestos felt applied spirally with a mechanical wrapping machine rotated by hand. This was a very successful example of a better way to apply a wrapper or shield since the old manual way, known as the cigarette method, was slow and cumbersome. Soon the use of asbestos wrappers over coatings became general. This system was a milestone in technical pipe line progress.

Other natural gas pipe line companies followed suit. To cite another example—in the winter of 1932-33 the Southern Counties Gas Company built a natural gas pipe line from Huntington Beach to San Diego, California. The coating specification of this line called for two sling applications of coal tar

Figure 6—Applying coal tar enamel near Amite, La., by the sling method to a line laid by the Louisiana Power and Light Company in the early thirties.

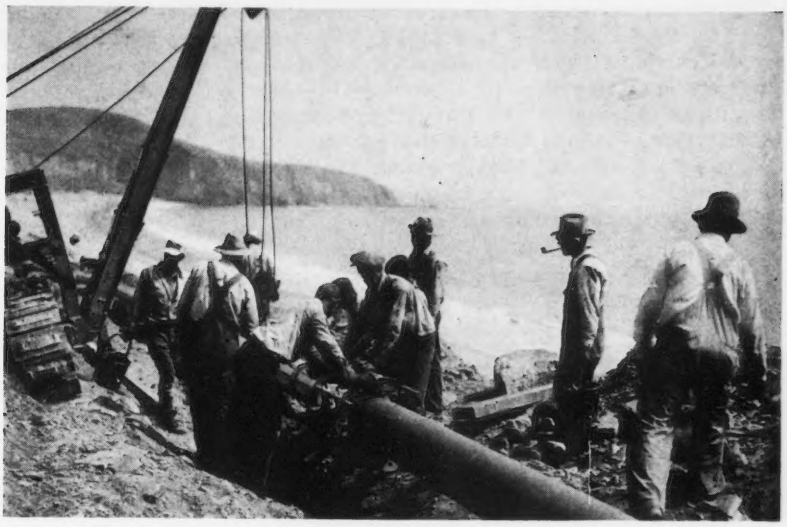

Figure 7—Another view of the Huntington Beach gas line to San Diego showing the use of spiral hand wrapping machine developed in the early thirties. This proved a great advance over the old manual operation. (See Reference at end of article.)

enamel followed by a spiral wrap of asbestos felt manually applied. The double application of enamel was designed to reduce the number of voids or "holidays" in the coating and the spiral shield of asbestos was to keep the coating from deformation and slippage. This important line is cathodically protected at low cost throughout its length and after fifteen years of service is showing no indication of pitting or corrosion.[1]

After asbestos felt had been accepted by the pipe line industry it was used almost universally with few exceptions, until 1938 when a new wrapper was placed on the market. This was an extremely light weight open mesh unsaturated glass mat or felt measuring only 15 mils in thickness. It was designed as a reinforcing material, or sandwich, between two hot applications of molten enamel and had the virtue of permitting the enamel to bleed through the interstices of the wrap.

The coating specification which a number of pipe line companies have adopted shown below is considered excellent but it must not be interpreted to mean that other types differing basically from this specification are not of proved value.

Coal Tar Enamel Specification

1. Mechanical cleaning and priming
2. Coal tar enamel 1/16" thick
3. One spiral wrap glass felt
4. Coal tar enamel coating 1/32" thick
5. One spiral wrap tar-saturated asbestos felt

Petroleum Compounds or Greases

Several large oil companies have experimented with petroleum greases and compounds, but have not placed them on the market commercially.

One company, however, has developed several grease-type coatings and wrappings which in numerous specifications have had broad acceptance in the oil and gas industry. This is true especially where small diameter pipe is used.

A number of specifications have been developed to cope with varying degrees of subsoil corrosivity and electrolytic activity which employ both hot and cold applications of coatings as well as impregnated reinforcing felts and shields, each of which has been designed to combat certain subsoil conditions.

These shields or reinforcing fabrics are worthy of special study because they can more nearly be termed "custom made" than many other shields and fabrics. These specifications, especially the ones employing both coatings and fabrics are applied in stationary machines which rotate and propel the pipe through coating and wrapping units joint by joint. Each joint is coupled to the following joint by a special coupling which lines up the pipe and assures an uninterrupted flow of pipe through the machine.

Bituminous Mastics

A number of bituminous mastics were developed during the twenties and early thirties. Of these it is believed only one is available commercially today. This is manufactured under patent and is applied by licensed applicators only.

This process is as follows: Prior to application of coating all pipe surfaces are shot-blasted. A hot coat of primer then is applied by spray or brush. This dries rapidly and the mastic is applied then by the extrusion process to the thickness of 5/16-inch to 5/8-inch depending on the diameter of the pipe.

Figure 8—An over-the-ditch travel machine. The complete coating and wrapping operation is done at one pass by this machine. A hot enamel coating and a spiral wrapping or shield is applied. This operation was in Brazoria County, Texas, between Bay City and Freeport for the Dow Chemical Company.

The mastic mix consists of a carefully proportioned aggregate and the correct percentage of asphalt (13 percent by weight) plus approximately 20 percent of lime dust and short-fibered asbestos. This mix is carefully blended under heat and then is extruded under pressure to pipe surfaces through the coating shoe to thickness noted. The equipment which applies this coating is stationary and all pipe is propelled and rotated through the machines.

When first introduced in 1936 this material was used largely where pipe lines traversed marshy land, lake and river bottoms. An economic advantage was claimed due to increased weight of coated pipe with consequent reduction of the number of river clamps or weights. However, with increased diameter of pipes increased buoyancy must be taken into consideration because the displacement of the pipe is greater.

Application Methods

There has been developed within the last few years a specialized industry for application of coatings to pipe. One division of this healthy and growing industry embraces central coating plant locations where practically all types of coatings are applied. These plants are designed especially for the purpose. Several have portable equipment for application in yards adjacent to the location of the pipe lines.

Central Coating Plants

A number of plants for coating application representing an investment of several millions of dollars have been constructed at locations adjacent to the pipe mills or at points distant from the producing mills but located in the transit flow line from the producer to the consuming territories.

The latest developments in this industry include heating ovens for warming the pipe before it is cleaned and dried, warming ovens for the primed pipe to speed up the drying of the primer and to insure that no moisture will be present on the primer when the enamel is applied. Other developments include steel-grit blasting cleaning methods, kettles equipped with mechanical agitators and with thermostats for close control of enamel temperatures.

The work is done under controlled conditions in these plants because the pipe is coated indoors where weather conditions do not jeopardize quality. By far the greatest percentage of all distribution pipe for water and gas lines is processed in central plants.

Yard Application

Yard applications are similar to central plant or mill applications with the exception that cleaning usually is done by machines used for field cleaning, and both cleaning and priming, and coating and wrapping procedures are subject to atmospheric conditions normal to outside exposures.

Field Application

Most of the large diameter transmission lines are coated and wrapped in the field using travel type cleaning and priming machines as well as travel type coating and wrapping machines. The coating and wrapping machines can coat and wrap using the single application of each material or can double coat and wrap applying the entire specification at one pass. Exceptions to using this type of application may occur during the winter months or wherever the right-of-way is too soft and marshy for the heavy machines to travel.

The latest development in field application equipment consists of cleaning and priming machines with neoprene treads fore and aft instead of the usual four steel tractions wheels. These treads are actuated and drive the machines down the lines in the same manner as the steel treads of a caterpillar tractor. This type tread does not injure the surface of the pipe due to the weight of the machines and prevents slippage down hills or when machines are winched up sharp slopes.

The same type treads are now in development for the coating and wrapping machines. Kettles with mechanical agitation now are available and also are being equipped with thermostats.

Conclusion

The mileage of working pipe lines in this country mentioned at the November meeting of the American Petroleum Institute in Chicago totaled 379,700 and as recalled the figures were compiled to include mileages in service as of June 1, 1947. Of the 379,700 miles, 60 percent of the pipe, or 230,000 miles, was in gas service. This mileage of pipe in the gas industry was in turn estimated to include 127,650 miles of small diameter pipe in cities and 102,350 miles of large diameter pipe used for transmission lines.

It is estimated that 70 percent of all the pipe now in service is protected and this includes pipe used within building walls for various types of conduits. Since the figures were compiled a year ago additional gas, crude oil, and products lines have been constructed just as fast as steel has been made available.

Within the next five years it is estimated that 19,000 miles of large diameter gas pipe lines will be constructed and this estimate is based on the applications made or pending for certificates of necessity and convenience. This is indeed a healthy outlook for the gas industry.

Late developments in coating materials, the fine application equipment now available, electrical inspection or testing, cathodic protection, and general know-how in combination has resulted in more nearly corrosion proof pipe lines for the gas and related industries.

Acknowledgement

Acknowledgment is made here to Stephen P. Cobb and R. G. Roberts for their invaluable assistance in preparing this paper.

Reference

1. N. K. Senatoroff, "Fifteen Years Experience in Application of External Corrosion Mitigation Methods to a High Pressure Natural Gas Transmission Line. *Corrosion*, 4, No 10 479-491 (1948) Oct.

High Temperature Corrosion of Metals*

By ANDREW DRAVNIEKS* and DR. HUGH J. McDONALD**

Introduction

With the development of new forms of primary machines such as gas turbines and jet propulsion motors, the interests of many metallurgists have been focussed on heat-resistant metals and alloys. A search is going on for materials which retain their good mechanical properties at high temperatures and possess good resistance against chemical attack by gases. This paper deals with problems concerning this form of chemical attack and presents some general ideas and new developments in the field.

Forms of Attack

ACCORDING TO a general principle of physical chemistry, metal can react with a gas only if the reaction will proceed with a decrease of free energy. This means that a metal can be attacked, with the formation of an oxide, only if the pressure of oxygen is higher than the dissociation pressure of the oxide.*** For instance, silver and platinum do not oxidize when heated in air because of the high dissociation pressures of their oxides. Unfortunately there is now no knowledge of any economically allowable and mechanically strong metals or alloys of this type. The most favorable case is nickel, with an oxide dissociation pressure of about 0.1mm of mercury at 2400° F. If oxide formation is thermodynamically possible, the actual rate of attack can vary widely and depends on many factors. The same is true for other metal-gas reactions.

Metals can react with gases in a variety of forms. First, the products of interaction can be either volatile or not. Volatile products obviously cause a detrimental attack and rapid destruction of the metal phase. Examples are tungsten at temperatures over 800° C in an oxygen-containing atmosphere, or iron in chlorine at 300° C or higher.

However, non-volatility of reaction products alone does not guarantee sufficient resistance of the metal to its environment. Non-volatile products form a scale on the surface of the metal, and the behavior of this scale substance may determine the further course of the reaction.

Two special cases may be considered at once. First, if a reaction proceeds under widely varying temperatures, the mechanical properties of metal and scale, adherence of the scale to the metal and the relative thermal expansion of metal and scale become important, and the shape of parts under attack may play a considerable role. The second case exists where a reaction already is proceeding at a rate sufficient to cause considerable accumulation of heat, so that either metal or scale melts and the reaction becomes violent—for example, iron burning in oxygen. More general is the case where, at constant temperature and reasonably slow reaction rates, the scale acts as a barrier hindering mutual access of metal and gas. Here, according to Pilling and Bedworth[1] two general cases may be distinguished: the specific volume of the scale formed is smaller than that of metal phase consumed, or the reverse. In the first case, generally the scale cannot cover the metal surface efficiently and the reaction is hindered only partially. The amount of attack is directly proportional to the time elapsed and therefore this form of metal-gas reaction is said to follow a linear or rectilinear time law. However, if the specific volume of scale formed is larger than that of metal phase consumed, the scale forms an effective barrier between the metal and gas. Reactants have to get into the scale and diffuse through the scale. Consequently, the processes at both scale-gas and scale-metal interfaces, and the process of diffusion through the scale, become rate-determining. The case is of great practical importance as the scale becomes protective under these conditions. However, different growth laws may be obeyed here.

Parabolic, Logarithmic and Asymptotic Growth Laws

The simplest case is where the protective action, i.e., resistance of the scale against passing of reactants through it, is directly proportional to the thickness of the scale. This is the situation[2] where

$$\text{Rate} = \frac{\text{Driving force}}{\text{Resistance}}$$

and, at any moment

$$dy/dt = k/y$$

y = thickness of scale, to which resistance is proportional

t = time

dy/dt = rate of increase of thickness

k = a constant for a given case and actually includes "some constant" times "driving force of the reaction." The latter depends on the properties of the scale and on the conditions of reaction such as gas pressure, temperature, etc.

Upon integration, the equation gives

$$y^2 = kt$$

where t is a measure of the time from the beginning of reaction on the bare metal surface. This is the parabolic growth law, first deduced by Tammann[3]. Every effect which disturbs the proportionality between thickness and resistance will cause deviation from the parabolic growth law.

Evans[4] pointed out that if additional diffusion barriers of any kind are formed in the scale, and if

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★ A paper presented at the Fifth Annual Conference, National Association of Corrosion Engineers, in Cincinnati, Ohio, April 11-14, 1949.

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*** In catalysis on metal surfaces, the surface is sometimes considerably roughened by interaction of gaseous substances and metal, although no detectable amounts of definite reaction product involving metal and gas are formed.

these barriers are statistically distributed and their probability is proportional to the thickness of the scale, another, the so-called logarithmic, law is arrived at:

$$y = k_1 e^{-k_2 t}$$

or

$$\log y = k_3 t + k_4$$

Some examples are the obstruction of diffusion paths[5] and cavities in the scale formed by release of internal stresses which develop during scale growth[6]. Logarithmic growth has been observed in the case of the oxidation of zinc[7] and stainless steel[8].

Finally there are cases where, for some yet insufficiently explained reasons, the thickness of the scale approaches, asymptotically, a certain value and then the growth comes to a virtual standstill; for example, the oxidation of aluminum at moderate temperatures. An explanation for the case of aluminum is put forward by Mott[9].

There are many instances where mixed laws are followed[10]. The laws considered briefly above have been derived by different workers in a number of ways.

Protectiveness of the Scale

The different time-scale thickness relationships provide for different rates of metal corrosion. In linear growth the scale grows at a constant rate, and the corrosion in ten hours is ten times that in one hour. In parabolic growth the corrosion in ten hours is about 3.2 times that in one hour. In logarithmic growth, the decrease in rate with time is usually still more efficient as usually the logarithmic growth constant is small; and in asymptotic growth, the corrosion comes to a standstill when a thin, hardly detectable film of reaction product is formed on the surface of the metal. Figure 1 represents these various growth laws in a graphical way.

In the case of parabolic growth, of course, the absolute value of the thickness developed in a given time depends on the magnitude of the constant k and may be quite different under different conditions. The logarithmic and asymptotic laws are the most desirable forms of scale growth from the standpoint of metal protection. Unfortunately, most metals at high temperatures (above 600° C) obey more or less generally the parabolic growth law or its variations (for alloys, see the work of Rhines[11]). Therefore the best that one can hope for is to obtain a metal with as low a parabolic growth rate constant k as possible, so that the scale grows parabolically but very slowly.

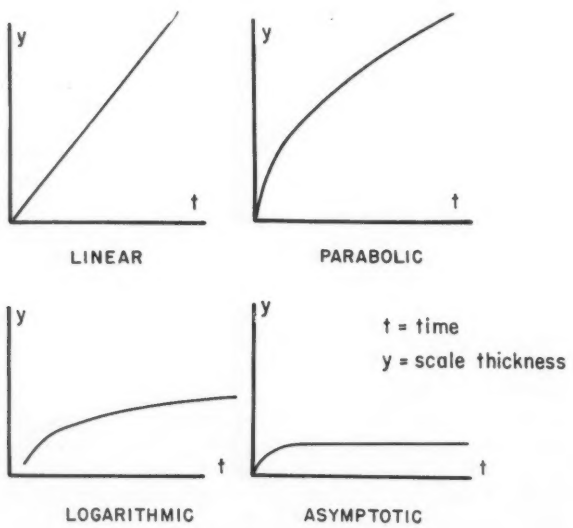

Figure 1—Graphical representation of the four laws governing scale growth in gas-metal reactions. Time is plotted on the x-axis and scale thickness on the y-axis.

Diffusion in Parabolic Scale Growth

The parabolic growth expression is the one obeyed most generally by metals at high temperatures and gas pressures, where there is a sufficient supply of reacting gas to form scale on the surface. The constant k, known as the growth rate constant, represents, however, an aggregation of many components which ought to be analyzed further. First, there is the driving force of the reaction, i.e., the drop in the chemical potentials of the gas or the metal across the scale. The driving force is the direct cause for diffusion through the scale. Secondly there are specific resistances to the diffusion, referred to unit thickness. Thirdly there are numerical factors necessary to bring about consistency in the units employed.

The specific resistance against diffusion perhaps may be considered more easily by thinking of the reciprocal of resistance, namely the permeability of the scale to the reactants. In simple terms, this would be the diffusion constant of the metal or gas in the scale substance; then the constant k in the parabolic equation will include the driving force, the diffusion coefficient and the adjustment of numerical constants

$$k = \text{Constant (Diffusion Coefficient) (Driving Force)}$$

The consideration of diffusion compels the investigator to consider at once the question about which many arguments have arisen and which is still being debated, namely, which component diffuses through the scale and in what form.

Diffusing Agent

Either gas or metal can diffuse through the scale and consequently the zone of scale growth may be either at the metal-scale or at the scale-gas interface. Simultaneous diffusion of both is also possible. Unfortunately, no systematic research has been done to elucidate this question for metals and alloys in general. A few specific cases have been investigated however. The usual techniques employed are marking the initial metal surface by scratches or foreign particles (Pfeil's method[12]), employment of a scale disk and metal disk in contact in the case of silver sulfide growth (Wagner[13, 14]) and more recently, radioactive tracers[15, 16]. It was found that iron and copper oxides, silver sulfide, copper iodide and silver halides grow by metal diffusion outwards. The parabolic law was obeyed in these cases. An unpublished investigation by the authors, using Pfeil's method, on the growth of nickel oxide at 1100° C gave an indication of diffusion of nickel through the oxide scale, in accordance with Wagner's views[17]. However, Valensi[18] and Arkharov[19] consider oxygen diffusion more probable in

this case. More work by the authors is under way on this problem. The halogen diffusion through lead halides on lead was connected with the formation of non-coherent loose scale[20]; in a peculiar case of catastrophic oxidation of molybdenum alloys described by Leslie and Fontana[21], Pfeil's method indicated oxygen diffusion and scale growth inward. These cases where the diffusion of negative components was observed simultaneously with the formation of a scale of undesirable properties as far as protectiveness is concerned, may indicate that even a favorable volume ratio (scale formed):(metal consumed) is insufficient to provide for coherent protective scale. Whether it is a general effect in the case of gas diffusion still is not established.

If the case of metal diffusion through the scale and consequent outward growth of the scale is considered, one must admit that as the scale grows outward some mechanism must act to transport metal atoms or ions from the metal phase to the scale. This is possible, for instance, by the continuous extension of the scale substance toward the metal phase which retreats. In this way the zone of metal phase consumption[22] becomes the stage of some complicated processes which are vital for scale growth. The extension of the scale in the form of columns toward the metal phase was observed first by Phiel[12]. Diffusion of gas through the scale to the metal is considered by Valensi[23] to be a frequently encountered process in oxide scale formation, occurring simultaneously with metal diffusion. Valensi proposes the diffusion of atomic oxygen.

A further matter of controversy has been the nature of the diffusing agent, namely, whether atoms or ions are responsible. Steric considerations as to the relative size of the corresponding particles and the lattice dimensions have been considered[24]. The most fruitful contribution here has been the electrochemical theory of scale growth introduced by Wagner.

Electrochemical Theory of Scale Growth

Wagner[13, 14, 17] was able to deduce the parabolic growth rate constant k from other properties of the scale substance, such as conductivity and free energy of formation. So far, his theory has been applied successfully in several cases. The fundamental assumptions of Wagner's theory are: the driving force of scale formation is the free energy change in the reaction

$$\text{Metal} + \text{Gas} \rightarrow \text{Scale}$$

Diffusion is actually a more or less independent migration of positive metal ions, negative ions derived from the gas, and electrons, all of which are charged particles. Therefore, their movement can be treated on the same basis as conductivity and ionic transference number data. In simple terms, Wagner's mechanism of scale growth may be visualized in the following way: The metal-scale-gas system is a galvanic cell with metal and gas electrodes, the electrolyte being the solid scale itself (see Figures 2 and 3). The solid electrolyte differs from an electrolyte in solution. Transport of current through the solution is performed only by ions. On the other hand, the solid electrolyte carries the current by means of ions

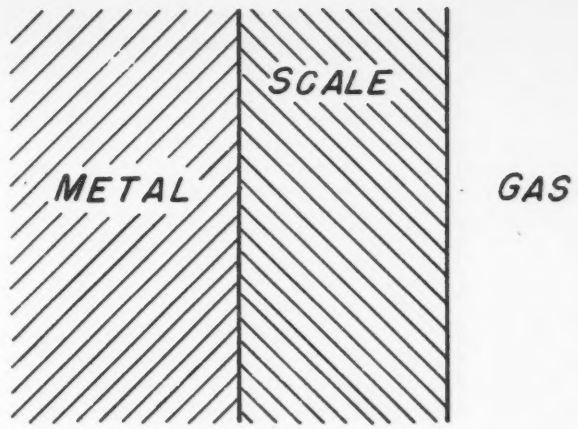

Figure 2—According to Wagner, the metal-scale-gas system may be considered as a galvanic cell with metal and gas electrodes, the electrolyte being the solid scale itself.

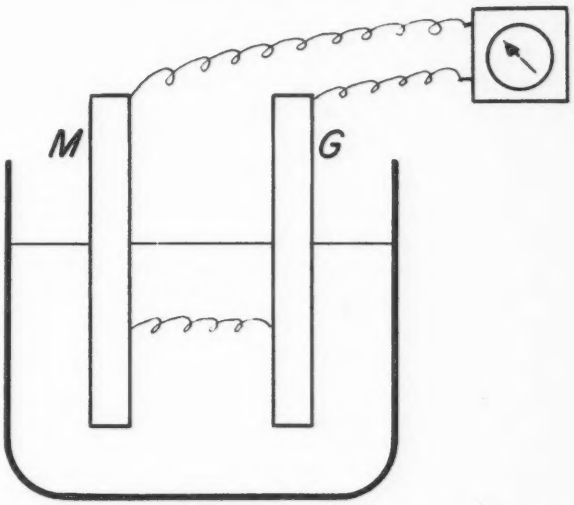

Figure 3—The solid electrolyte carries the current by means of ions and electrons, the participation of these particles varying widely for different substances. In general, there is always some electronic transport, which may be symbolized by a thin wire connecting the electrodes.

and electrons and, depending on the substance, the participation of these particles in the current transport may vary widely. For instance, current through solid silver chloride is carried chiefly by silver cations; in solid lead chloride current is carried by chloride ions and in solid oxides of different metals prevalently by electrons. In general there is always some electronic current transport. This electronic transport may be symbolized by a thin wire connecting the electrodes in the cell of Figure 3. Elementary electrochemical considerations show that in this case the potential between the two electrodes is lowered in accordance with the electronic conductivity of the scale (that is, the electrolyte); the potential gradient under which the ions of metal or gas in the solid scale electrolyte can migrate is correspondingly changed. The subject has been treated mathematically in a number of different ways[13, 14, 17, 25, 26].

The general equation for the parabolic growth rate

constant k in the equation $y^2 = kt$ is then obtained in the form

$$k = \frac{(n_1 + n_2) n_3 \kappa E_0}{F}$$

where

n_1 = fraction of current carried by cations in scale
n_2 = fraction of current carried by anions in scale
n_3 = fraction of current carried by electrons in scale
$n_1 + n_2 + n_3 = 1$ (n = transport number)
κ = conductivity of scale substance
E_0 = potential of the cell formed by the reaction
Metal + Gas = Scale
under the particular conditions of the reaction.
F = Faraday (96,500 coulombs)

The equation has been tested by Wagner and coworkers in a few cases, e.g., copper + oxygen. The scaling rate constants were obtained experimentally. On the right hand side of the equation, E_0, conductivity and transport numbers were obtained by other means, and k was calculated by employing the above expression. The results agreed as to the order of magnitude, which is considered good support for the theory.

If the cell in Figure 3 is considered, one can see that the electronic transport inside the scale electrolyte (corresponding to the "size" of the wire) lowers the potential set up between the electrodes. Dravnieks and McDonald[20] succeeded, in several cases, in actually measuring the potentials developed by the scaling reaction across the scales and these potentials were found to be in fair agreement with the values calculated from the free energy values and ionic transport data in the corresponding scales. The mere fact that it was possible to detect the potentials is convincing evidence for the validity of the electrochemical theory of scale growth.

The scaling process as viewed by the theory is described then as a succession of several steps. A metal atom, considered univalent, from the metal phase enters the lattice of the scale as a separate cation and electron. Both migrate to the surface of the scale. There electrons meet the adsorbed gas, e.g., oxygen atoms, and form oxygen anions. Oxygen anions combine with the arriving metal cations and new lattice units of scale substance are deposited. A corresponding picture can be devised also for the case of gas diffusing into the scale and to the metal-scale interface.

Disorder Theory of Diffusion in Solids

A further elaboration of the electrochemical theory attempts to explain the mechanism of diffusion of ions and electrons through solids in general, as the diffusion process is usually the rate-determining one in the case of scaling reactions. The details cannot be considered here. However the main points are: The disorder theory of solid lattices as developed by the works of Schottky, Frenkel, Wagner and others, describes the lattices as mostly regular arrangements of ions or atoms; however, there is always some degree of irregularly placed ions or atoms such as ions in positions between the regular lattice points, holes in the places where ions should be, and ions with charges other than those expected for the prevailing stoichiometric composition (e.g., some cupric ions in a cuprous oxide lattice). These places of disorder represent higher energy concentration than the average for the lattice, and the actual extent and mode of disorder depends on the amount of energy requisite to form different kinds of units of disorder. The regular lattice units are in thermodynamic equilibrium with displaced ions or charges. A well-known example of disorder in cuprous oxide lattice is shown in Figure 4. Deviation from stoichiometric composition (formation of so-called solid solutions of oxygen or metal in the oxide) is the direct consequence of the disorder structure. The disorder theory, as introduced into scale growth processes, states that the particles which migrate are the displaced ions and charges. For instance, in the case of cuprous oxide (Figure 4), the ions diffuse by going into adjacent holes and the electrons by moving from a cuprous ion to an adjacent cupric ion.

The rate of diffusion and scale growth depends on the number of disordered positions and the mobility of the individual position in the lattice. Generally it is assumed that the mobility does not change appreciably with the change in the concentration of disorder positions, although the order of mobility can be very different for different substances and lattice types.

As the extent of disorder depends on the thermodynamic equilibrium between disorder positions and the normal lattice, it is evident that changing the chemical potential by change of gas pressure of one component of the lattice, e.g., oxygen, will shift the equilibrium and change the concentration of disorder positions. Therefore the change in oxygen pressure should change the diffusion rates and conductivities; the direction and amount of the effect can be predicted semi-quantitatively for different types of disorder. The effect has found experimental proof in a few cases[17]; an important conclusion is that the scaling rate depends on gas pressure. The number and mobility of disorder positions will increase with temperature, thereby causing the increase in scaling rate with temperature.

Despite the simplicity of its concepts, the disorder and electrochemical theory of scaling suffers from a serious lack of pertinent physicochemical data and constants. The electrochemical theory is of little value in the case of metal oxides which are electronic conductors with very low ionic transport numbers. It seems that the power of the theory is low in explaining scaling processes of most metals in oxygen, and the electrochemical theory offers no advantage here over other simple diffusion theories.

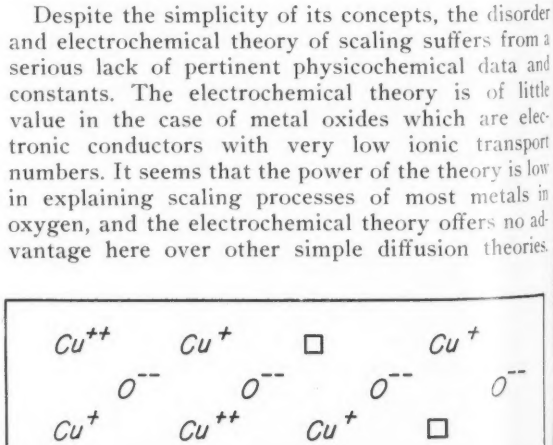

Figure 4—Form of disorder proposed for cuprous oxide in an oxygen-containing atmosphere. The lattice contains some holes or vacancies in places where cuprous ions might be expected to be present. If electrical neutrality of the whole lattice is to be maintained, some cupric ions must be present.

The concept of disorder positions in solid lattices seems more promising and is certainly due to gain ground in investigations in scaling. The lack of data on regions of solid solutions: metal + oxide and oxide + oxygen at different temperatures over wide ranges of pressures of oxygen is the major obstacle in this connection.

Other Theoretical Developments

Many theories and additions to theories have been proposed since Pilling and Bedworth[1] and Tammann[3, 27, 28] in the early twenties developed the foundation for the scientific approach to scaling reactions. As most interesting, developments by Mott[9], Evans[6] and Gulbransen[29] may be mentioned. Mott dealt with thin film of alumina on aluminum and proposed several explanations for apparent stoppage of film growth after reaching a certain thickness, and his main consideration concerns the effect of space charges built up by oxygen ions on the surface of the film; the theory applies to low temperatures and is less interesting in the case of advanced scaling at high temperatures. Evans proposed an accumulation of stresses in the scale with increasing thickness and pointed out that, depending on the cohesion forces of scale and adhesion between scale and metal, either cracks through the scale normal to the metal surface or blisters with cavities parallel to the metal surface can be formed. The latter can hinder the diffusion of metal through the scale outward. The authors believe this theory would have to be modified by a consideration of conditions in the zone of contact between the scale and the metal[22].

Gulbransen has applied the theory of reaction rates developed by Eyring, Laidler and others[30], to the diffusion in scale growth. From rates of scaling reactions at different temperatures, obtained by use of an elaborate microbalance technique, he calculated the free energies and entropies of activation. However, thus far no further successful correlations have been derived from these formally calculated constants.

Conditions of Reaction and Scaling Rates

Different factors which influence the rate of scaling will be considered briefly in this section.

Temperature

Temperature generally increases the rate of scaling reactions. The increase is roughly 1.2 to 2.0 times per 10° C (18° F) temperature increase if the temperature differences are not too large and the scaling is of practical importance, i.e., not extremely slow. Thus the same thickness of scale on a certain steel in air has formed in 10 minutes at 1000° C as in 120 minutes at 800° C. This does not apply to temperatures where a new oxide phase may appear. For instance, the appearance of an FeO phase in the complex oxide scale on iron, which occurs at ca. 550° C, causes appreciable acceleration of scaling because of the high permeability of the FeO lattice to iron ions. At low temperatures the adsorbed oxygen layer on the surface of the metal does not form an oxide phase and the scaling does not start at all. At very high temperatures the reaction can sometimes pass into combustion with melting of the metal or scale.

The appearance of a spinel type oxide lattice (e.g., Fe_3O_4) has been correlated successfully with high oxidation resistance of underlying metal. However the explanation has not been given as to why certain mixed spinels are much more protective than others. A very fundamental piece of work on lattices of oxide films has been done by Hickman and Gulbransen[31, 32, 33] employing electron diffraction techniques, and this is still in progress.

Pressure

The pressure of oxygen, in the case of oxidation, acts differently in various pressure ranges. At very low oxygen pressure, the dissociation pressure of the oxide scale may be higher than the external oxygen pressure. Then the scale does not form. When the pressure exceeds the dissociation value, scale forms. If the absolute concentration of oxygen (number of oxygen molecules in the gas phase) is very low, the scale may not receive a sufficient amount of oxygen because too few molecules of oxygen impinge and are accommodated in the adsorbed layer of oxygen on the surface of the oxide[34] (but compare also[35]). Then the rate of oxygen adsorption is rate-determining and the scaling rate varies widely with change of oxygen pressure. This may be important at pressures well below 1mm of mercury, and certainly not higher than several mm of mercury. At all ordinary pressures the rate depends on the fourth to the eighth root of the oxygen pressure, in fair agreement with consequences of disorder theory, and therefore is not important from a practical standpoint. This is an explanation for the observation that scaling of iron in air, dry steam, or carbon dioxide does not differ very much. In dry steam and carbon dioxide it is the oxygen formed by dissociation which is responsible for scaling. Whether atomic oxygen is important is not yet established. The question is under investigation by the authors. At high temperatures the changes in oxygen pressure become increasingly important. Oxidation rates at high oxygen pressures have not been investigated so far. It is interesting to note that the oxygen pressure changes can make certain oxide phases thermodynamically possible or impossible and so influence the scaling rate in an indirect way by changing scale composition.

Rate of Flow

The rate of scaling usually does not change with the rate of flow of gas if the gas is pure oxygen. If a gas mixture or gas producing oxygen by dissociation (steam or carbon dioxide) is employed, the flow rate becomes important. Oxygen from the mixture reacts with metal and the non-reacting constituent accumulates in the neighborhood of the scale, blocking the access of fresh oxygen. Flow removes the stagnant layer and greatly increases the rate of scaling. Two- to four-fold differences have been recorded and flow rates up to 60 feet per minute have been employed to assure reaching a region of constancy, where the rate of scaling does not change with further increase in flow rate[36, 37, 38]. The flow factor has

been disregarded in many investigations; obviously, very pure oxygen must be employed to avoid complications arising in stagnant atmospheres[39]. An extreme example of difference in corrosion rate and even form has been demonstrated recently by Fontana[21]. No known investigations have been performed on oxidation at extremely fast flow rates.

Presence of Other Substances in the Gas Phase

Undoubtedly, various vapors and gases influence the rates of scaling if present in the gas phase. Thus, small contaminations of sulfur in combustion are ruinous[40] and cause a pitting form of attack. Here, probably, is a fruitful field for speculation based on disorder theories. However, very little systematic quantitative investigation has been done in this direction. Dunn[39] reported that 7.5 parts of HCl in oxygen increases five-fold the scale growth rate of copper, and chlorine cannot be detected in the scale. The interesting fact that chromium is plated out of chromium chloride vapor on iron at 1000° C[41] indicates that many surprising effects may be expected from thorough exploration on the effects of contamination in the gas phase.

The scaling in steam, carbon dioxide, nitrogen dioxide, etc., may be considered as scaling in the oxygen formed by the thermal dissociation of the corresponding gases. The presence of water vapor does not influence the scaling in air at high temperatures appreciably, although minor yet unexplained effects have been reported.

Compound Metal Systems

Alloys have been investigated by Rhines, Smirnov and others[10, 42, 43, 44] and well-developed theories explain many effects in the oxidation of alloys. The most important facts to bear in mind are: if an oxide is present in a closed system without an additional supply of oxygen, and another metal is placed in the same closed system, then it may happen that the first oxide will dissociate giving off oxygen and the second metal will oxidize. A necessary condition is that the dissociation pressure of the first metal (say nickel) oxide be higher than that of the second (say iron). Therefore it is possible, e.g., to find nickel metal in globules imbedded in the iron oxide scale on iron. Another fact is the ability of many metals, e.g., copper, nickel, etc., to dissolve oxygen. If the metal contains an alloying component whose oxide has a very low dissociation pressure, this oxide can be formed in the body of the base metal, taking oxygen from the oxygen solution in the metal. An elegant treatment by Rhines and co-workers[11] establishes the conditions for the formation of external and internal scales in alloys. A further complication in the oxidation of alloys is the mutual solubility of metal oxides and formation of mixed phases.

Preferential oxidation of an alloying constituent, e.g., chromium in chrome nickel, often causes considerable changes in the composition of the remaining metal, for example, exhaustion of the chromium content of long-heated chrome nickel wires. The high temperature oxidation resistance of stainless steel is attributed to a formation of chromium oxide containing oxide scale which possesses low permeability for ions.

Surface Conditions of Metal

The treatment of the surface of a metal before the oxidation has a profound influence on the initial phase of scale and, to some extent, influences also the later behavior of the scale. The initial surface conditions determine the orientation of formed oxide crystals, and often it has been found that crystal planes of metal and oxide are co-oriented[45, 46, 47]. As the thickness increases, the coordination is lost, but frequently the layer formed at the start still retains its peculiarities and by virtue of its location in the way of diffusing ions still exhibits an influence on diffusion rates.

If single crystals are investigated, e.g., copper [48, 49, 50, 51], it is found that different faces of the crystal oxidize at different rates.

Varying Temperature

Changes in temperature during scaling can cause cracking of the scale and acceleration of oxidation. Cracking depends to a considerable extent on the shape of the specimen, e.g., the scale on metal strips cracks much easier than on round cylinders. However in some cases it has been found that the change in temperature does not introduce any complications; for instance, Bourggraff[52] reports that total scaling of iron in the temperature range 800-1300° C under changing temperature can be calculated using the principle of additivity. It seems that for thin oxide films the additivity can exist only for mechanically strong and adhering scales. Systematic investigations in this direction undoubtedly would yield interesting and practically important results.

Summary

Due to the recent developments in jet-propulsion engines, rocket-type motors and gas turbines, there is a re-awakened interest in heat-resistant metals and alloys. A search is underway for superior metals which will retain their mechanical properties at elevated temperatures and, in addition, exhibit good resistance to chemical attack by combustion gases. A number of general characteristics which play an important role in determining high temperature resistance of alloys include volatility of the reaction products, adherence of the scale to the metal, the relative thermal expansion and specific volume of metal scale, etc.

The different "time-scale thickness" relationships result in different rates of metal corrosion. These may be classified according to whether they follow a linear, parabolic, logarithmic or asymptotic growth law. In linear growth the scale grows at a constant rate; in parabolic growth the corrosion in 10 hours is about 3.2 times that in one hour; in logarithmic growth the decrease in rate with time is still more efficient; and in asymptotic growth the corrosion comes to a standstill when a very thin film of reaction product is formed on the surface of the metal. Although the logarithmic and asymptotic laws are the most desirable forms of scale growth from the standpoint of metal protection, most metals obey the parabolic growth law.

Either gas or metal can diffuse through the scale and therefore the zone of scale growth may be either at the metal-scale or at the scale-gas interface. A matter of controversy has been the nature of the diffusing agent—whether ions or atoms are responsible. The most fruitful contribution has been the electrochemical theory of scale growth introduced by Wagner. An elaboration of the electrochemical theory attempts to explain the mechanism of the diffusion of ions and electrons on the basis of the disorder theory of solids. Other theoretical developments which are considered include the effect of various factors such as pressure, rate of flow, presence of foreign substances in the gas phase, surface conditions of the metal, and variations in temperature, on the course of the reaction.

Acknowledgment

The experimental program on this problem of reactions of gases with metals at high temperatures is being supported by the Office of Naval Research.

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Principles of Writing Specifications For Metal Protective Paints ★

By W. W. CRANMER*

GOOD ENGINEERING practice demands that constants and variables be recognized and segregated. Once this is done, the constants may be dismissed and attention focused on the variables.

If paint is a part of any corrosion prevention program, then the quality of that paint becomes a constant only by specification. Or, more exactly, paint quality approaches a constant depending on the effectiveness of the specification and its enforcement.

Instances are known where large industrial companies have tried to assay the effectiveness of their maintenance painting program, only to find that they were using so many different proprietary paints for the same purpose that a reasonable analysis of the situation was impossible. This may be of no importance if the company is not interested in obtaining full return for every dollar spent. However, most companies are extremely interested in dollars—especially those which are being spent.

Material purchase specifications have been discussed by Ashkinazy[1], and the use of paint as an engineering material has been described by Mattiello[2]. Both papers indicate that engineers accord paint a considerably greater emphasis than was customary a few years ago. For example, Ellaby[3] wrote as follows in 1940: "In the beginning, in common with possibly many other engineers, it appeared to me that painting was one of the relatively unimportant things which was a finishing touch to the important and carefully constructed structure. Therefore, relatively slight consideration was given to the materials comprising the paint . . . "

Between Ellaby's paper in 1940 and Mattiello's in 1946, and as a natural consequence of the war, paint specifications were issued by government departments at an almost feverish rate. Some engineers began their acquaintance with specifications at that time. However, certain raw material specifications appeared as early as the turn of the century. The author is indebted to Mr. E. F. Hickson[4, 5] of the National Bureau of Standards for the brief historical review which follows.

"The 'father' of paint specifications in this country is the late Dr. Charles B. Dudley, formerly chief chemist for the Pennsylvania Railroad. He is credited with publishing, in 1890, the first modern systematic studies of paint materials. Dr. Dudley was president of the American Society for Testing Materials beginning in 1906.

"Other early investigators followed his lead. These include such men as George B. Heckle, Robert Job, G. W. Thompson, Frank P. Ingalls, Maximilian Toch, S. S. Voorhees, John Dewar, Percy H. Walker, H. A. Gardner, C. D. Holley, E. F. Ladd, J. A. Schaeffer, A. H. Sabin, P. C. McIlhiney**, and many others.

". . . The Navy Department published specifications for both white lead and japan drier in 1906.*** Navy Department specifications for drop black, black paint, and ultramarine blue were issued in 1901. Likewise one for paste wood filler was issued in 1902. Specifications for raw and boiled linseed oils were issued in 1903. Navy Department specifications for aluminum powder and copper paint were issued in 1908. These examples of Navy specifications are believed to be among the oldest of those put out by government agencies.

"When the United States entered World War I, the Government needed immense quantities of paint materials and had no standard specifications, the specifications for a given material intended for the same use being different in the various branches of the service. The paint committee of the War Industries Board realized the necessity for standardizing Government specifications and was making such satisfactory progress when the war ended that it requested the Secretary of Commerce to continue this work. As a result of this request, there was organized in February 1919 an Interdepartmental Committee on Paint Specification Standardization which, in cooperation with producers, prepared a number of specifications and recommended their use by all Government agencies . . .

"In 1921, the Bureau of the Budget organized the Federal Specifications Board, and in the same year the technical committee on paint was formed. From 1921 to 1937 the chairman of this technical committee was Percy H. Walker. From 1937 to date the chairman is E. F. Hickson. This committee has turned out over 100 specifications covering paint, varnish, lacquer and related materials."****

Despite the large number of paint specifications now available, and the work and worry which has

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★ A paper presented at the Fifth Annual Conference of The National Association of Corrosion Engineers in Cincinnati, Ohio, April 11-14, 1949.

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** Also active in this connection was Robert S. Perry.

*** The Navy Department also published specifications for paints and turpentine as early as January, 1901.

**** A recommended booklet on this subject is "Paint Manual with Particular Reference to Federal Specifications," BMS 105. Percy H. Walker and E. F. Hickson, issued October 1945. It is available from the Superintendent of Documents, Washington 25, D. C., price $1.00.

been expended, no perfect specifications are yet available. By perfect specification is meant one which is "a concise, definite, and complete statement of what the buyer requires from the seller."[6] It is not unusual for a leaflet specification to consist of ten to twenty pages of printed matter, which is certainly not concise.

A busy engineer confronted with the necessity of studying twenty pages of fine print is entitled to consider that he is abused. His position is simply that he wants a paint capable of protecting a given structure for a certain period of time. This is at least concise—and would be both definite and complete if it were not for some regrettable ignorance on the part of some paint technologists.

First, there is no quick test which will predict the service life of a paint. If there were, the public could be protected from sub-standard paints which enjoy a brief popularity, often at high prices, as a result of unsupported and unethical advertising claims. In the absence of a quick test, there appears to be no way to specify an exterior metal protective paint except on the basis of experience and composition. This is a time-honored and successful method. Knowingly or unknowingly, the engineer uses this method when he says "red lead in oil," is "zinc yellow in phenolic varnish." Here, the engineer uses past experience concerning successful painting jobs and correlates this experience with a statement about composition. Present Navy specifications for exterior paints do exactly the same thing, but more formally.

For example, the gray hull paint used on combat vessels is described by Navy specification 52P45c. It consists of four essential parts, as follows:

1. A formula which lists raw materials as to kind and quantity.
2. A set of requirements, numbering twenty-two in this instance.
3. Directions for sampling.
4. Test methods.

Such a specification represents the culmination of much work. In the ideal case, this work started with consideration of raw materials and the preparation of experimental formulations which were tried out by making small panel exposure tests. Again considering the ideal case, the best formulas from the exposure tests were used in actual service trials. Assuming that several formulas survived the service trials, final selection of a single formula is governed by availability, cost, ease of handling, or relative toxicity of ingredients. Once all this work is done, actual specification writing is relatively easy. Actually, what results is really a description of a formula rather than a true specification.

The heart of this specification is in the formula, which lists each raw material, both as to exact kind and quantity. The seller needs little more than this information to determine what to do and how much to charge. He will need some direction as to processing, and for this reason fineness of grind and viscosity requirements are added. If the appearance of the dry paint is important—and this is not the case when metal protection only is considered—he must be instructed as to color and gloss. If the paint will require thinning in use, he may further have to meet a compatibility requirement. This leaves the necessity for listing a formula and about five requirements—hardly enough to account for the ten or twenty pages of printed matter mentioned earlier, or even to account for the 22 requirements mentioned in one specification.

The excuse for the many requirements is that they provide a means for determining whether the formula has been followed. These requirements must go along with detailed test methods, either listed as to sources or written out in detail. By this explanation, it becomes apparent that much of the specification is given over to matters involved in large scale procurement, covering how samples shall be taken and tested. This part of the specification is like a policeman. Because he is there, laws can be enforced; so, the sampling and testing procedures provide the means for enforcing the specification. Few people need the policeman. Likewise, in practically all buyer and seller relations good ethical conduct is the rule, and both parties are anxious to fulfill their obligations. However, it would not be good business for a manufacturer to agree to meet requirements unless he knew how his product was to be tested, and a great deal of work has been done to standardize test methods and eliminate disputes as much as possible. Actually, refinements in test methods during the past ten years have been gratifying indeed, especially as to measurements of those characteristics, such as color difference, which once were considered purely subjective. In some cases such matters are reported now in completely objective, physical, and quantitative fashion.

The formula type specification is easy for the manufacturer because he must simply assemble and process a stated set of ingredients. It is efficient for large scale purchase, especially during emergency periods like the recent war, because the procuring agency can focus its attention on a known list of raw materials. Thus the effect of any expected shortages can be anticipated in advance, and adjustments made before the coatings industry is badly upset.

This type specification is sometimes criticized because it tends to produce a static condition. The background necessary for producing good specifications of this type, as outlined previously, requires years of work. If one were starting today to develop all the necessary background knowledge, then the outlook would be very discouraging indeed. But this is never true. A respectable amount of knowledge is available already, and more continuously is being assembled. There is no reason to think that this situation will change, especially as long as new materials are being developed and promoted as replacements for competitive materials.

A more serious criticism is that otherwise good raw materials may be neglected simply because they did not happen to be a part of the selected formula-

tion. Attempts to correct this matter have led to some hybrid specifications where a formula is proposed, but not rigidly fixed as to kind and quantity of ingredients. This loose formula is then bolstered by appending a **control formula** to the specification. The control formula is used as a guide, and as a comparison testing standard, but apparently is not otherwise binding on the manufacturer.

It should be clear that the author has a personal bias toward composition type paint specifications. This is natural, since procurement of ship paint for the Navy was organized successfully and controlled by this means during the war. However, it is sincerely hoped that true performance specifications for metal protective paints will be developed. This task should not be considered impossible. But it cannot be achieved without resolving to support patiently the necessary work until this goal is attained.

Briefly, an adequate performance specification, as Reinsmith[7] has so well stated, "can be prepared only when all the desirable characteristics of the material are known and are definable, and when accurate short term tests for these characteristics are known." It is possible that some work now started will provide the needed short term tests. The type of investigation being done by D. M. Williams and others[8] on weathering machine correlation is an example of the kind of information which must be obtained before it can be certain that a short test can be relied on to give precise information about what would happen in actual use.

If one were to attempt a paint specification without restriction on composition, it appears that reliable short term tests would be needed for the following characteristics:

1. Expected durability.
2. Adhesion and retention of adhesion.
3. Storage life.
4. Moisture vapor permeability.
5. Consistency (or some measure of suitability for application).
6. Ability to restrain corrosion.
7. Retention of appearance.

Expected durability might be measured by some means such as change in electrical characteristics. This is not a new idea and much promising work has been reported.[9] It is also a possibility that expected durability might be measured by a combination of other tests, such as retention of adhesion and appearance coupled with ability to restrain corrosion. Recent activity[10] on quantitative measurement of adhesion should be followed by studies of change in adhesion under conditions designed to accelerate breakdown.

While a reliable short term test for expected durability is not a Utopian dream, it does appear now to be a matter of the very indefinite future. So corrosion engineers will be well advised to continue their present long-term testing programs, and to purchase those formulations which have proved their durability in actual service. Likewise, they should be warned continually that a specification at best can only control the quality of the paint. The quality of the paint job is controlled by the care given in cleaning and pretreating the metal, and in applying the paint. These factors are easily five times as important to ultimate durability as is paint quality.

The opinions expressed in this paper are those of the author and do not necessarily reflect the opinion of the Navy Department.

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TECHNICAL PAPERS PROCEDURE

All papers submitted for publication in CORROSION are reviewed by the Editorial Review Committee, or specialists selected by that committee to review the papers. Suggestions of reviewers as to desirable additions or revisions are submitted to the author, who is given the opportunity to make the suggested changes. The paper in final form is accepted or rejected according to the judgment of the committee and the Editor of CORROSION. When the author can substantiate his viewpoint and prefers not to follow the suggestions of the reviewer and the overall paper merits publication, the author's wishes are followed.

The Role of Adsorption from Solution In Corrosion Inhibitor Action ★

By DR. NORMAN HACKERMAN* and HAROLD R. SCHMIDT**

THE USE OF POLAR organic substances and colloidal materials as corrosion inhibitors has been investigated for many years and wide application has been found for them, especially in acid solutions. In general there is little disagreement that these materials function essentially by treating the metal surface. The first step in the mechanism almost always has been described in terms of adsorption of the inhibitor molecule from solution onto the metal surface. There is, however, considerable variance in opinion as to the function of the adsorbed molecule thereafter in retarding corrosion.

A number of workers postulate that the effect is one which may be described best as a "blanketing" action. Mann and his co-workers[1] discuss the amines and certain positively charged colloids in terms of their migration to the cathodic areas of the metal where they become attached, probably by virtue of the electrostatic forces. They maintain that the effectiveness is related to the area covered by the molecule and point out that those molecules which are inclined from the normal to the surface are apt to be more effective due to increased coverage. Certain irregularities observed with secondary and tertiary amines are explained by them on the basis of stearic hindrance. The adsorption is discussed in terms of the Langmuir theory and mention is made of the important factor that the time lag of the molecule on the surface in a sense a measure of the firmness of adherence, is a function of the surface forces and the basicity of the amines. Lawrence and Walton[2] agree with these ideas and offer additional evidence in support of them. These papers show curves for the effectiveness of inhibiting action versus inhibitor concentration (in terms of percentage nitrogen) which are typical adsorption isotherms.

A few investigators prefer to consider the second step in the sequence as one which causes an increase in hydrogen overvoltage at the cathodic areas. Cathodic polarization curves for metals in corrosive media containing organic compounds have been obtained which show increasing cathodicity with increased current density and the curves were displaced to more cathodic values with greater inhibitor concentration. This was ascribed to a rise in hydrogen overvoltage due to the adsorption of the organic molecules at the cathodic areas. In the event this is the mechanism it would be necessary that the cathodic potential should not exceed the reduction potential of the adsorbed material. It is interesting to note that the cathodic potential of steel in normal sulfuric acid at 25° C decreased with increasing concentration of inhibitor when no current was impressed. Table I gives these values for quinaldine ethiodide from the work of Chappel, Roetheli, and

TABLE I
The Effect of Inhibitor Concentrations on Potential Steel, 1 N H_2SO_4, 25° C.

Gram/Liter of Quinaldine Ethiodide	Cathode Potential (No Current)	Anode Potential Decrease (No Current)
0.00	0.8828 volts	0.0000 volts
0.001	.....	0.0091
0.10	0.8761	0.0148
0.40	.....	0.0207
0.70	0.8571	0.0293
1.00	.....	0.0307
2.00	.....	0.0299

McCarthy[3] who found that the anodic potential decreased also with increased inhibitor concentration. The latter is a true adsorption effect but it would appear that the former is not because the potential would not become more anodic with greater inhibitor concentration in the absence of an externally impressed current, or else the molecule reacted with the metal after adsorption or removed previously adsorbed materials from the anodic areas. Certainly because small local cells flourish on the metal surface the inhibitor should migrate to cathodic areas even when no current is flowing through the cell. It is possible the inhibitor molecule in this case normally is to be found on the anodic portions of the coupon as well as the cathodic areas. Warner[4] agrees with the theory of increased hydrogen overvoltage for organic bases but says other types of compounds are more likely to induce passivity at the anode. In the University of Texas laboratory it has been possible to effect inhibition with some organic acids in air-free acid solutions containing steel and by any theory of selective adsorption these materials should be found at the anodic areas.

Rhodes and Kuhn[5] postulated that the formation of a film, again at the cathodic areas, increased the cell resistance and thereby provided protection. Although they were able to measure such increases in resistance they found no quantitative correlation between this value and inhibitor efficiency. Machu,[6] however, maintained that when the film resistance reaches a value of about 3 ohms, maximum efficiency

★ Voluntarily presented for publication May 31, 1949. A paper presented at the University Conference on Corrosion and Material Protection, in Chicago, Ill., in June 1947.

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or corrosion retardation was obtained regardless of the inhibitor concentration.

A number of workers,[2,6,7,8] go far in clarifying an important aspect of the mechanism in pointing out that adsorption generally is not limited to any specific area of a solid surface. That is, the inhibitor may be adsorbed on any portion of the metal surface and the inference may be drawn that such adsorption may be firmer at some places than at others. This is a factor of greatest significance which does not seem to have been considered seriously until the last few years. Mayne[9] talks of adsorption of undissociated salts of metals at anodic areas wherein the inhibitor becomes effective by smothering the most actively dissolving area of the metal surface. Erbacher[10] cites work to prove that cation adsorption also takes place on anodic areas. Machu[6] makes clear his belief that adsorption may take place over the whole surface and most actively at the anodic areas. He believes the "pin-cushion" effect produced increases the cell resistance by decreasing conductivity due to the fact the ions have to travel through relatively long, narrow channels between adsorbed molecules. Uhlig[11] distinguishes between "passivators" which he believes are strongly adsorbed on the metal surface and which diminish the activity of the metal, and inhibitors which presumably act only to reduce the rate of penetration of corrosive elements to the metal surface.

A Generalized Theory for the Mechanism of Organic Corrosion Inhibitors

It may be conceded that organic inhibitors are effective by virtue of their attachment to the metal surface. The adherence may, however, be considered to be due to purely physical forces or to the relatively stronger chemical forces. It may be argued of course that there is no fundamental difference between the two types of bonds but the fact remains that in practice it is possible to distinguish between chemisorption and physical adsorption from a knowledge of the heat of adsorption, the ease of reversibility the temperature coefficients, and the rate of adsorption.

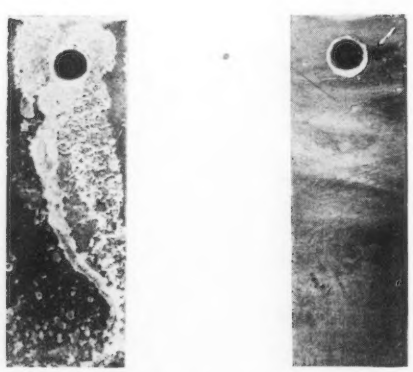

Figure 1—A—Effect of 200 ppm acetic acid solution on steel, oxygen absent. B—Effect of addition of 50 ppm of naphthenic acid (based on hydrocarbon present) on corrosive action shown in A.

In either case the adsorption takes place through the polar group, or groups, to the metal surface and covers the surface more or less completely when present in sufficient concentration. The requirement that adsorption takes place primarily at the cathodic areas seems to be too specific to be in accord with the general theories of adsorption. It may be argued that with the metal surface showing areas of positive and negative charge any positively charged ions would tend to congregate in the latter region. This is true of course and means that adsorption of the positive ions is greater at these points due to increased local concentration. To this extent, at least, the theories depending on cathodic adsorption are effective. Nevertheless adsorption also should occur at the anodic areas and in so doing play a role in reducing corrosion process rates.

There are numerous examples of corrosion inhibitors which give rise to negatively charged particles. For example, inhibition of acetic acid attack on steel in an anaerobic system has been obtained in this laboratory by the use of naphthenic acid or by the iron and manganese soaps of this material. Furthermore, Manchu[6] has stated that sulfur-containing molecules, formaldehyde, and other materials forming negative ions are effective inhibitors. He also pointed out that gelatine in solutions of pH on either side of its isoelectric point (i.e. with either a negative or positive zeta potential) is adsorbed on iron to approximately the same extent.

Aside from the *extent* of coverage, the *type* of coverage is important in determining the effectiveness of inhibition. In the case of physically adsorbed substances the inhibiting effects result primarily from the decreased ability of the corrosive molecules to reach the metal surface. This may appear as an increase in film resistance, or hydrogen overvoltage, or may be considered simply in terms of a diffusion controlled reaction rate. The chemisorbed molecule, on the other hand, not only duplicates the effect of impeding the corrosive material but also decreases the tendency of the metal atom, to which it is attached, to leave the metal surface, as Uhlig[11] has pointed out. An added advantage in this case is that the adsorbed molecule is not as easily removed or re-dissolved. There are numerous data and observations in the literature which, taken together, plausibly may be interpreted as indications of the existence of chemisorption processes in the functioning of organic inhibitors. For example, specificity of inhibitor action frequently is mentioned but is not readily explainable on the basis of the theories already proposed. It should be noted that chemisorption processes are specific in nature whereas physical adsorption is, within limits, independent of the nature of the adsorbate and adsorbent. An analogy may be made to chemical reactions as contrasted to physical condensations.

A characteristic of physical adsorption processes is the fact they take place instantaneously provided the adsorbate has free access to the solid surface. There are a number of instances reported in which a definite time lag is noted. Rhodes and Kuhn[7] meas-

ured the resistance of an adsorbed film, and they reported an increase in this resistance occurring over a period of 15 to 30 minutes. Table II, using data from that paper, illustrates this effect for steel-sulfuric acid systems with phenylacridine and acridine respectively as inhibitors. More directly, a number of investigators[1,5,8,12,13] report an increase in

TABLE II

Rate of Increase of Inhibitor Film Resistance with Time

0.05 per cent carbon steel, 7.5 per cent H_2SO_4, 10 millimoles of inhibitor per liter.

Time (Minutes)	Phenylacridine	Acridine
0.16	0.72	....
0.5	0.73	0.96
1.5	....	1.18
2.0	....	1.29
2.5	....	1.37
3.0	....	1.44
4.0	....	1.49
5.0	....	1.59
7.0	....	1.73
10.0	0.79	1.79
15.0	0.80	1.82
20.0	....	1.83

effectiveness of certain inhibitors over a short period of time after they had been added to the system. Further in one of the papers cited,[8] it was stated that stirring on addition of an inhibitor to the system decreased its effectiveness but that stirring a few minutes after the addition of the inhibitor to the unagitated system did not produce this effect. It must be admitted the time lag may be attributed to the period required for diffusion of the inhibitor molecule to the surface as well as to the time needed for orientation of the molecule before it adsorbs. Nevertheless, this effect must be considered in relation to chemisorption, particularly when taken in conjunction with other effects to be mentioned below.

Information on the heats of adsorption of organic compounds which function typically as inhibitors is meager and indirect. In a film lubrication study Frowing[14] determined the heats of adsorption of a number of polar organic molecules on steel by calculation from experimental values of coefficient of friction. Some of these values are reproduced in Table III. There are sufficiently large differences

TABLE III

Heats of Adsorption of Various Polar Organic Molecules

Compound	△H (Calories)
Methyl stearate	8600
Ethyl stearate	3900
Butyl stearate	3200
n-hexyl stearate	6900
n-octadecyl stearate	4900
Octadecyl chloride	14500
Octadecyl iodide	7500
Octadecyl cyanide	4300
Octadecyl thiocyanate	4700
1-Nitrooctadecane	13000
Caproic acid	12500
Myristic acid	13000
Stearic acid	13000
Oleic acid	13500

between these values to show that some of the materials are held to the steel surface by considerably stronger bonds than others are. In this connection, Armbruster and Austin[12] found measureable differences in heats of adsorption (and in adsorption isotherms) for vapor phase adsorption of ethyl iodide on reduced and reduced steel surfaces.

Experiments showing an increased effectiveness of inhibition with increasing temperature, or maxima in the temperature coefficient of inhibition, are not explained readily by current inhibitor theories. On the basis, however, that the extent of chemisorption may either increase or decrease with an increase in temperature, whereas physical adsorption always exhibits a negative temperature coefficient, such effects are more readily understood. Tables IV and V, using data from the literature[13,15] illustrates this not uncommon effect.

TABLE IV

Effect of Temperature on Inhibition of Steel in 1 N H_2SO_4

Inhibitor	Temperature °C.	Ml. H_2 Evolved
Starch	25	50
	72	65
Fish Glue	25	25
	72	10
Carpenter's Glue	25	25
	72	9

TABLE V

Effect of Temperature on the Retardation of Corrosion by Inhibitors Steel, 1.0 per cent $CuSO_4$, and 0.1 per cent agar as inhibitor

Temperature °C.	Percent Retardation
1	54
8	54
21	71
35	57
50	45
65	37
80	31

It has been mentioned above that the ease of resolution of the adsorbed inhibitor should vary with the nature of the adsorption bonds. Although there is not very much information in the literature to draw upon, some experiments performed by Mann, Lauer, and Hultin[1] show very clearly a difference in the ease with which adsorbed inhibitor molecules can be removed. These data are collected in Table VI. Additional experimental evidence of such differences will be offered below.

TABLE VI

Desorption of Some Amines

Adsorption System: Steel, 1 N H_2SO_4, 0.1 per cent inhibitor as N_2, 25° C., 46 hours.

Corroding System: Steel with adsorbed amine, 1 N H_2SO_4

TIME (Hours)	PER CENT PROTECTION		
	n-diamyl amine	n-dibutyl amine	n-triamyl amine
0	99.26	98.4	99.31
4	99.21	96.9	99.24
8	99.19	92.7	99.20
16	76.72	74.8	99.09
4	Scrubbed, Washed and Repeated		98.72
8			79.24
16			71.32
40			59.67

The fact that such generally unexplained data as cited above can be made to appear reasonable on the basis of the nature of the sorptive forces leads to

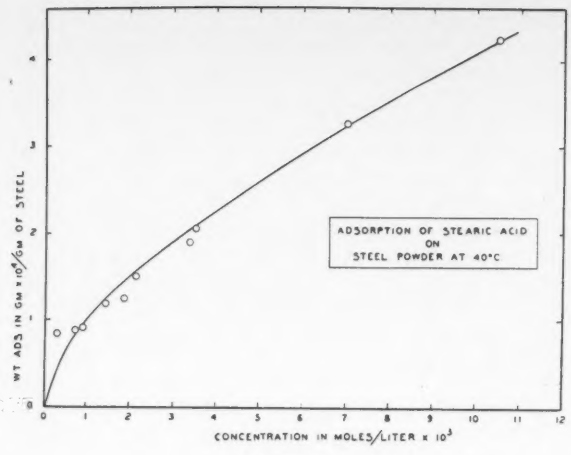

Figure 2

the conclusion that chemisorption must be considered a factor in corrosion inhibition by polar organic molecules. Granting that chemisorption may take place in such systems as are being discussed here, maximum inhibition would be obtained in the event the entire surface were covered by molecules held by chemical forces. The metal would be less likely to dissolve then because a) the activity of each atom on the surface would be decreased, b) the corrosive agent would be retarded in its approach to the surface, and c) the inhibitor would not be removed easily by re-solution in the surrounding liquid. An interesting aspect of the last item is the use of organic inhibitors in systems containing both aqueous solutions and liquid hydrocarbons. Although removal of inhibitors from the metal when used in acid pickling baths is not a serious factor, it may be the controlling factor where organic solvents are present, particularly with systems in which there is continual renewal of pure solvent.

The possibility exists that those substances which are likely to be chemisorbed on the metal are sufficiently active to act as corrosive agents themselves. Thus, consider the variation in effect of the fatty acid series. The lower members definitely are corrosive to steel. For example, Figure 1 showed the effect of acetic acid. The higher ones (e.g., stearic acid) do not react but are adsorbed. Figure 2 shows an adsorption isotherm for stearic acid on steel powder. Furthermore, the protection provided by chemisorbed substances may be destroyed by other agencies such as increased temperature of subsequent chemical reaction. For example the naphthenic acid experiments mentioned above when run in the presence of air with no acetic acid present produced a very high rate of penetration on the steel. It has been assumed that this change was the result of oxidation of the quasi-compound of iron and the naphthenate radical, to a ferric soap which hydrolyzed, precipitating ferric oxide and reproducing the naphthenic acid to repeat the cycle.

In real systems it is necessary to accept the fact that the metal never is covered entirely by chemisorbed inhibitor molecules. Instead it is more probable that the more active portions or "spots" are so affected while most of the remainder of the surface is covered by inhibitor held by the weaker physical forces. Since the latter coverage is reversible more readily it follows the inhibitor must be renewed continuously, particularly if there is continuous flow of the liquid past the metal. These portions of the surface which are covered by the physically adsorbed molecules, however, should be less active and therefore the metal loss from these areas normally would be less. Some metal will be lost in all cases, and in this connection the analogy of a paint film to a "leaky" condenser[16] may well apply.

Theories of adsorption never have required that total coverage be obtained on solid surfaces even when the latter is essentially saturated. In the case of relatively close-packed organic molecules, however, lateral forces between the hydrocarbon chains can function to provide additional protection. In systems containing hydrocarbons, and also with commercial inhibitors containing inert materials, nonpolar molecules can in fact be oriented and incorporated in the adsorbed film, thereby providing more complete coverage. Of equal importance is the fact that such forces operating betwen neighboring physically adsorbed and chemisorbed molecules should reduce the tendency of the former to re-dissolve. The magnitude of such lateral attraction would be of the same order as those causing physical adsorption. Thus such a mechanism should provide a) coverage for portions of the surface on which adsorption does not occur and b) increased difficulty of removal of the less firmly held inhibitor molecules from the surface.

It is interesting to consider the effect of the subphase on the adherence of such films. It now is widely appreciated[11,17,18] that corrosion resistance is related to the nature of the metal structure. A recent paper[9] points out that reaction may take place between an atom of the solid surface and a dissolved particle to give a product which is stable only so long as it remains on the supporting solid lattice. Supporting evidence is supplied for this statement by work reported in the field of ore flotation by Taggart,[19] who speaks of metathetical reactions between dissolved substances and the solid surface. His work shows that the solubility of the substance so formed on the surface is altered by the solubility of the substrate—for example the solubility of copper sulfate on the surface of copper sulfide is low in spite of the rather high solubility of bulk copper sulfate. This information is also further evidence that chemisorption may be an important factor in corrosion inhibition. It is suggested here that because of the thinness of the inhibitor films and the fact any pseudo-crystals they form will be "soft," such inhibitors are more likely to accept the deformities caused by the subphase without undue strain and splitting.

The principal point to be made, perhaps, is that a study of inhibitors should be approached from the viewpoint of a fundamental knowledge of their properties. Austin and Armbruster[12] already have made such a proposal with regard to relating inhibiting action of organic molecules to dipole moment and

polarizability. Others, including Mann and his coworkers, have made similar suggestions. In the University of Texas laboratory an attempt is being made to study the inhibitor substances from the viewpoint of adsorption-desorption isotherms, the structure of the material after it has been placed on the metal, and the characteristics of the inhibitor materials in forming thin films on a clean water surface.

Experimental Investigations

Adsorption isotherms have been run at 40° C for stearic acid, stearyl alcohol, succinimide, di-butyl thiourea, and p-aminobiphenyl, and others are now in progress.

Two methods have been used. The first consists simply of shaking a benzene solution of the inhibitor with a weighed amount of powdered steel and removing aliquot portions of the solution, after equilibrium has been attained, for analysis. The analytical method poses a serious problem but in the case of the substances mentioned above it was possible to evaporate the solvent and weigh the residue. The experiment continues by adding an equal aliquot of a more concentrated solution to the system from which the sample had been removed and repeating the process.

The second method consists of packing a glass column with steel powder and providing the column with inlets and outlets for any required liquids or gases. The column is jacketed to allow for temperature control. In this system it is possible to flow the inhibitor solution through the powder under a variety of conditions and determine the amount adsorbed from the concentration of the effluent. A corrosive liquid then can be passed through the column and the extent of protection from corrosion can be obtained by analytical methods. Following this, pure solvent may be passed through and the extent of desorption determined. Finally, the corrosive may be put through once more. This system offers considerable possibilities as a means of estimating inhibitor characteristics under many conditions.

For purposes of desorption, pure, dry benzene was added to the steel powder (using either method) after the original solution was removed and the procedure described above then was reversed.

Of the substances studied to date only the stearic acid gave measurable results. Figure 2 gives the adsorption isotherm and Figure 3 the desorption

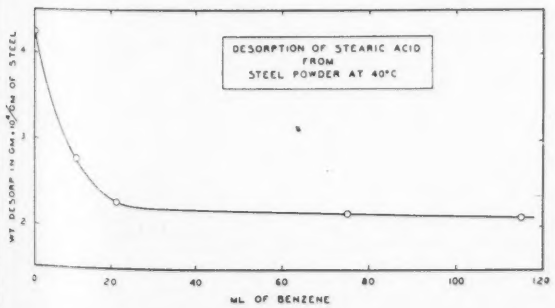

Figure 3

Figure 4—Electron diffraction patterns, by reflection method, typical of organic compounds which are highly oriented on steel surfaces.

isotherm for the system. It is apparent the solvent treatment did not remove all adhering stearic acid. This suggests that a small portion of the material is held so firmly it cannot be removed readily, i.e., is chemisorbed. It is possible, of course, that an iron soap was formed which is not soluble in the benzene. Frowing,[13] however, states that such a reaction does not occur. Also, other evidence is offered below to support the contention that stearic acid does not desorb completely from the steel.

Electron diffraction studies of metal surfaces which have been treated by a number of polar organic substances and commercial inhibitors have been carried out. The instrument used in this work was an RCA electron microscope with an electron diffraction attachment. The accelerating voltage was 50,000, which corresponds to a wave length of about 0.05 Å to be associated with the electron beam. For accurate determination of the spacings on the patterns obtained, the instrument was calibrated using the sodium chloride pattern. The value of $L\lambda$, for use in equation $d = \frac{L\lambda}{r}$, was found to be 1.19×10^{-6}.

The metal surface on which the inhibitors were placed was a highly polished, 5 x 5 mm square of 2 mm thick SAE 1020 steel sheet. An adaptor was built to contain these coupons in the diffraction port of the electron microscope. It was possible to tilt or rotate the coupon so any angle with respect to the electron beam was obtainable. Organic liquids were put on the surface generally by placing a few drops of the substances on the coupon and removing the excess with lens paper. The coupons were placed in a desiccator under an atmosphere of dry, natural gas until the diffraction patterns were taken. An attempt also was made to adsorb the various materials from solution in benzene. A difficulty presented itself in that on removing the coupon from the liquid, a drop of the solution remained on the surface and apparently laid down a film in a manner analogous to evaporation of a solvent from a solution. Attempts which were not especially successful were made to remove this drop. Solid substances, e.g. stearic acid and stearyl alcohol were melted on the steel surface or were adsorbed from solution. It should be noted that there was no evidence of a pattern from the surface of the prepared, but untreated, steel coupon.

These studies showed it is possible to get definite evidence of structure of some of the attached mole-

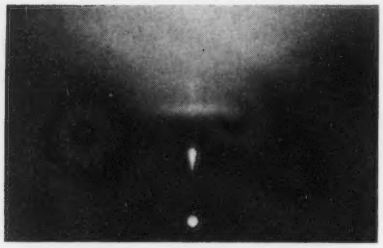

Figure 5—As for Figure 4 showing another type of orientation.

Figure 6—As for Figure 4 but for material showing little or no lateral orientation.

Figure 7a and b—Electron diffraction pattern, by reflection method, of naphthenic acid on steel before and after desorption treatment.

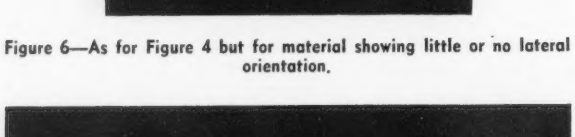

Figure 8a and b—Same as Figure 7 for a commercial inhibitor.

cules. Figure 4 shows a structure typical of naphthenic acid, cyclohexylamine, palmitic acid, a commercial inhibitor, and a high boiling fraction of hydrocarbon condensate from some gas wells. The structure is similar to that given by applied polylayers of barium stearate as described by Germer and Storks.[20] Lateral orientation is marked. Measurement of the band distance gives a value of 2.51 Å between planes and is assumed to be due to alternate carbon atoms in the hydrocarbon chains. Thus, there are well defined, two-dimensional crystals formed. Figure 5 shows a structure due to cetyl alcohol. From the weak band running at an angle to the stronger diffraction spots it is believed these molecules are inclined from the normal and again well-defined crystals are present. This pattern is similar to that for applied polylayers of stearic acid as reported by Germer and Storks.[20] Figure 6 is typical of a commercial inhibitor* which has as its principal constituent a ring compound containing a nitrogen atom and two carbonyl groupings. Stearic acid, fused while on the steel surface and then allowed to cool, gave the same pattern. Karle and Brockway[21] have made calculations relating band separations to the randomness of the angle the molecules may have with respect to the normal. From the separation of the "halos" of Figure 6 the deviation from the normal approximates 20°. It is clear there is little or no lateral orientation in this case as compared to the substances giving the patterns shown in Figure 4 or 5.

An adaptation of the technique described above was used as a means of determining the type of adsorption encountered with the various substances on steel. By treating the surface in the manner described and obtaining an electron diffraction pattern one finds only that some specific structure obtains. The material may merely be deposited on the surface, however, or it may actually be adsorbed. The ease with which it can be removed by simple washing with pure solvent should give evidence of the firmness with which it is attached to the surface. In practice, the steel surface was treated initially with the compound and an electron diffraction pattern obtained. Then the coupon was removed, washed twice with pure hydrocarbon (Skellysolve B was used in most cases), returned to the diffraction camera, and a second picture was obtained. Figures 7a and 7b show the patterns obtained with naphthenic acid before and after the desorption treatment. It is evident the inhibitor has been removed and that during the period it was there it had etched the steel surface because the pattern shown in Figure 7b is that of iron. In contrast Figures 8a and 8b show that in the case of the commercial inhibitor used in this experiment no change has taken place as a consequence of the washing with the solvent and evidently the material is held firmly. It was found also that stearic acid was not desorbed by a dilute (100 ppm) solution of the acid in Skellysolve B. Cyclohexylamine, however, was desorbed completely by the pure solvent. This method of study certainly gives direct evidence of the ease of desorption of alleged inhibitors from the metal surface.

Two other points in connection with these patterns should be made. First, scanning of the surface shows no variation in patterns of the type shown in Figure 4. Thus, in Figure 4 the molecules are perpendicular to the surface within a few degrees. Second, the pattern in Figure 7a is not the same as shown in Figure 4 although both are due to naphthenic acid (from the same bottle of the material). The difference lies in the fact that the former pattern was taken

* Kontol 115, obtained through the courtesy of the Tretolite Company, St. Louis, Mo.

within thirty minutes of the time of application of the naphthenic acid whereas the latter was taken 36 hours after application. It is apparent there is a time lag in attaining the final oriented state. If the coupon treated with naphthenic acid only a short time previously is exposed to the electron beam for an appreciable period, the more ordered pattern is obtained. This is taken to indicate that the hysteresis is lessened, as a result of heating by the electron beam. Regardless of the type of pattern obtained for the naphthenic acid, however, the material is desorbed readily as described earlier and in every case leaves an etched steel surface.

Force-area relationships of some of these inhibitors have been investigated using a Cenco hydrophil balance. This initial attempt was made in order to explore possible differences in such relationships for various inhibitors. Three commercial inhibitors were spread on a clean water surface and the force-area curves obtained in the normal manner. See Figure 9. Kontol 115, which is the one that was strongly adsorbed because it was not desorbed by a hydrocarbon wash in experiments described just above, showed the largest film pressure before collapsing. It also appears to be converted quickly to the condensed state as indicated by the sharp rise in the curve. The break in the curve apparently corresponds to the transition from the L_e or LS to the S state described by Harkins.[22] It is interesting to note that this substance has shown considerable promise in treating high pressure natural gas condensate well corrosion. The second inhibitor,* which shows some similarity to inhibitor A in its force-area relationships, is known to be effective in laboratory experiments. The third was naphthenic acid and no evidence was found for the formation of a condensed state even at very low areas. With this material hydrocarbon was squeezed out almost continuously as the area was decreased. Possibly the polar materials in this commercial sample were in very low concentration.

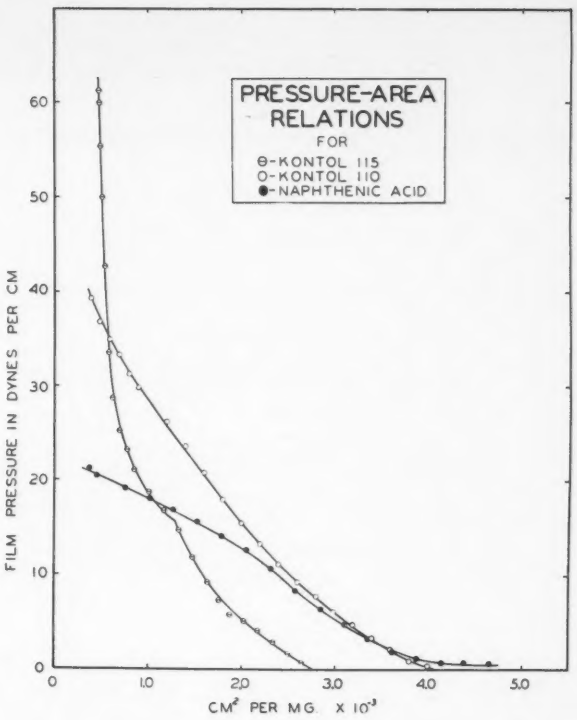

Figure 9

* Kontol 110, also supplied by the Tretolite Company.

Acknowledgement

The authors take this opportunity to express their deep appreciation to the Corrosion Research Project Committee of the Natural Gasoline Association of America for its financial support and encouragement of this work.

In addition, the authors are happy to acknowledge the valuable aid given them by L. L. Antes, Department of Electrical Engineering at the University of Texas, in the use of the electron microscope.

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Destruction of an Admiralty Tube Bundle By Stress Corrosion In the Presence of Mercury

By B. B. MORTON*

The destruction of an exchanger tube bundle by stress corrosion in the presence of mercury was brought to this correspondent's attention by a metallurgist of a large petroleum refinery. The bundle was stated to contain several hundred tubes 5/8-inch diameter, 20 feet long, of 14-gauge Admiralty metal. Nearly all of the tubes were ruined as a result of the introduction of the mercury into the tubes.

The cold inlet stream makes several passes through the tube bundle of this exchanger and the hot overhead material passes on the shell side and exchanges heat with the incoming stream. It is estimated that the metal of the tubes operates at about 300° F.

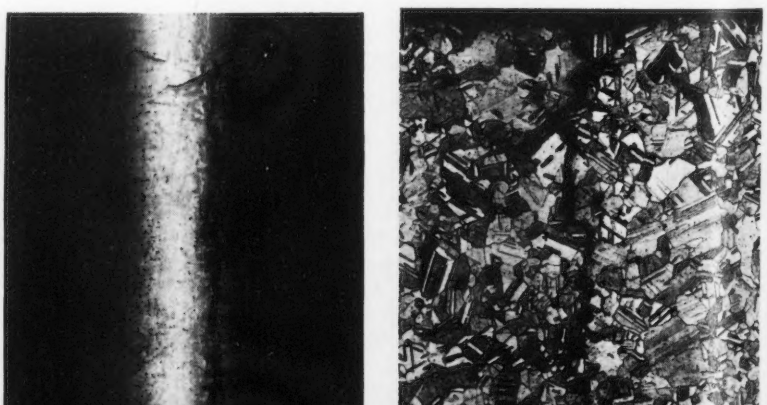
After several hours of operation, it was noted that the tubes were leaking and the bundle subsequently was withdrawn. It was found that the tubes were cracked extensively and in many directions. The white appearance of the inside of the tubes was such that the first report of the failure was to the effect that the tubes had suffered "decoppering." An examination in the laboratory indicated that mercury was deposited on the metal which was quite brittle. Globules of mercury were evident in the cracks and mercury could be distilled from the tube metal.

A search for the source of the mercury led to the examination of the inlet line and the source was traved to a seal-pot which had been installed on the inlet line in connection with a metering device. The mechanism by which the mercury was transferred from the seal-pot is not clear nor is it clear at the moment as to how a repetition of the accident can be wholly prevented. A trap is to be installed in the line and it is hoped that this will entrap any future mercury carried from the seal-pot. However, too great faith is not placed in this method of protection as the stream may convey, mechanically, finely dispersed mercury particles.

While it is recognized that the cracking of Admiralty in the presence of mercury represents no new contribution to the knowledge of corrosion, it is felt that the recital of the above may warn others against a costly repetition of the accident.

For those interested in the mechanics of stress cracking of brass in the presence of mercury, the "Symposium on Stress Corrosion Cracking of Metals" ASTM-AIME-1944, is suggested. It is interesting to note that a high order of stresses in the metal often is considered essential for the mechanics of stress corrosion in the presence of mercury to assert itself. In this case it is felt that the very high order of stresses required hardly could have existed. Some contribution to the level of stresses necessary for such failure may result from a further investigation of these tubes.

Typical Stress Corrosion Crack



(Left)—Typical stress corrosion crack in an Admiralty metal tube (actual size). (Right)—Cross-section (magnification 100X) of a typical stress corrosion crack in an Admiralty metal tube. (Photographs courtesy Scovill Mfg. Co.)

* Development and Research Division, International Nickel Co., Inc., 67 Wall Street, New York, N. Y. Correspondent for Non-Ferrous Metals, Corroson Magazine.

NACE News

Deadline on Amendment Ballots Is July 14

North East Region Will Vote on Adding Member of Board from Each Section

The board of trustees of North East Region met May 19 at 4 Irving Place, New York City.

Among other business transacted, the following decisions were reached:

Secretary-Treasurer L. B. Donovan was instructed to proceed with balloting on the pending proposed amendment to the regional by-laws by which the board of trustees would be increased by including one officer from each section in the region.

Succession of regional officers was discussed, and because it was indicated further amendment of by-laws would be required, the problem was tabled to a later date.

A request for a statement of policy regarding section financing from the executive secretary was authorized.

The board also was of the opinion all correspondence between Central NACE Office and Sections should clear through the regional secretary-treasurer.

Secretary-treasurer Donovan was authorized to advise R. H. Coe of the Pittsburgh Section the board preferred an early fall region-section NACE meeting instead of one proposed for June 10 to be held jointly with The Electrochemical Society.

A notice will be included in the next general mailing to region membership asking individual members to communicate directly with section officers requesting regular programs of meetings. In this way it is expected the question of geographical boundaries between sections may be resolved.

W. E. Shaw, chairman of the Metropolitan New York Section, announced future meetings of his group would be held Sept. 28 and Nov. 9, 1949 and February 8 and May 10, 1950. This is a change from dates previously announced.

Sections will be requested to have an officer attend future regional meetings under the interim trustee plan.

R. H. Lynch has agreed to see what can be done to develop sectional organizations in New England.

Houston Section heard James Gow, chief metallurgist of the Electric Steel Foundry, Portland, Oregon, formerly affiliated with Batelle Memorial Institute, present a paper on "Hot Gas Corrosion of Iron-Chromium-Nickel Alloys," illustrated with numerous slides of specimens and test results. Mr. Gow has been engaged in corrosion work for about 19 years.

This was the last section meeting until September.

DR. F. N. ALQUIST

Chairman of the Editorial Review Committee, succeeding Dr. Paul Bachman, resigned. Dr. Alquist, is a research chemist for the organic research division, The Dow Chemical Company, Midland, Mich. His field includes metal corrosion inhibitors, corrosion problems, water type deposits and oil field chemical problems.

Shreveport Section's June 9 meeting at the Caddo Hotel, Shreveport, was featured by the presentation of a motion picture, "Coating and Wrapping Operations," presented by F. E. Rolston, Dearborn Chemical Co. Twenty-three members and guests attended. Next meeting of the section is in September.

Mailed from Central NACE office in Houston to all active, associate and corporate members of the association has been a letter ballot, action on which will determine the changes to be made in the association's articles of organization. The ballot includes all of the changes incorporated in a similar mailing to membership before the Cincinnati conference. Changes incorporated into this official ballot represent suggestions for modifications which were collected during deliberations at the conference.

Following is a brief summary of the issues to be voted on:

1. Four alternative amendments to Article III.

2. Amendments 2 to 9, inclusive, which are to be voted on collectively.

3. Amendment 10, which is new text for present Article II.

The general purpose of the amendments is to make the organization more responsive to the will of the membership and in the case of Amendments 2 to 9, specifically to alter the language of the articles in such a way as to remove discrepancies and ambiguities.

A. B. Campbell, executive secretary of the association urges members to execute, sign and return the ballots to the Houston office not later than July 14, 1949.

North Texas Section's new officers, elected at a business meeting and dinner May 27 atended by 18 members and guests at the Blackstone Hotel, Fort Worth, are as follows:

Chairman, K. D. Wahlquist, Electro Rust-Proofing Corp., Dallas, Texas; Vice-Chairman, J. R. Ligon, Sinclair Pipe Line Co., Fort Worth, Texas; Secretary-Treasurer, J. L. Poole, Magnolia Pipe Line Co., Dallas, Texas; Assistant Secretary-Treasurer, N. H. Simpson, Consolidated Vultee Aircraft Corp., Fort Worth, Texas. Next meeting of the section is scheduled in September.

NEW CORPORATE AND ASSOCIATE MEMBERS

Following is a list of new Corporate and Associate Members who have joined NACE during the period from May 15, 1949, to June 15, 1949, bringing to 270 the number of these types of Association memberships:

	Representative
Dowell, Inc., Tulsa, Okla.	Guy F. Williams
Gulf Oil Corp., Port Arthur, Texas	D. L. Burns
Shell Development Co., Emeryville, Cal.	Aaron Wachter
Stone & Webster Engineering Corp., Boston, Mass.	Edwin B. Powell

Corrosion Short Course Set Sept. 12-16

Official Registrations Are Being Taken Now

Letters received from all parts of the United States indicate a widespread interest in the proposed "Short Course on Corrosion," tentatively scheduled for September 12-16 at the University of Texas, Austin. Originally a project of South Central Region, initiated by Nathan Schofer, now with Ebasco Services, New York, the growing interest in the project outside the region led to assumption of financial responsibility for the course by national NACE. Preliminary surveys of potential attendance indicate the course has assumed an importance beyond the normal scope of a regional activity.

Arrangements for the course will be facilitated by receipt from persons interested in attending, the informal notice included on the page with this article. This notice does not constitute a committment to attend the course, it was pointed out, but is merely a means whereby potential attendance may be estimated. Formal registration blanks will be sent out later to those who express interest and willingness to attend.

Dr. Norman Hackerman, University of Texas, who has been working actively with officers of the region and with national NACE officers on the project, has outlined several alternate schedules of activity. It has been decided the course will be directed principally to people in industry who must deal with corrosion problems but who have not had the experience or background to do so efficiently. Dr. Hackerman says the course will be useful as a refresher in the fundamental phenomena with which the corrosion of metals is concerned.

Plan of Course

The plan of the course has been outlined as follows:

Nine two-hour lectures followed by discussion periods will be given. Two lectures will be devoted to background, such as considerations of pertinent aspects of thermodynamics, kinetics and electrochemistry.

The remainder of the lectures will be devoted to detailed consideration of corrosive processes and corrosion prevention.

Experience and knowledge of authorities in several fields will provide the basis for recognition of corrosion types. Efficient prevention practices will be discussed.

Selected motion pictures paralleling or elaborating on the subject matter of the lectures and discussions are being considered for the afternoon period. A decision about the showing of films and final scheduling of this part of the program will be announced later. The program was designed without lecture periods during the afternoon because of climatic conditions at Austin, which in the summer, militate against close and effective attention by students.

Housing is Provided

Housing for 170 on the university campus has been made available. The cost per person per night for these accomodations will be $1.50. Rooms will be ready for occupancy Sunday, September 11 and must be released by noon, Friday, September 16. Registration fee for the course has been set at $20.

Restaurant facilities should be plentiful because the university will not be in session.

Further information and official application blanks about the course will be available by request from A. B. Campbell, Executive-Secretary, National Association of Corrosion Engineers, 905 Southern Standard Building, Houston 2, Texas.

TENTATIVE SCHEDULE
SHORT COURSE IN CORROSION

University of Texas, Austin
September 12-16, 1949

Monday		
Sept. 12—	9:00-12:30 p.m.	Fundamentals
	7:30-10:30 p.m.	Fundamentals
Tuesday		
Sept. 13—	9:30-11:30 a.m.	Metallurgy
	7:30-10:00 p.m.	Types of corrosion
Wednesday		
Sept. 14—	9:00-11:30 a.m.	Corrosion resistant metals
	7:30-10:00 p.m.	Protective coatings
Thursday		
Sept. 15—	9:00-11:00 a.m.	Cathodic protection
	7:30-10:00 p.m.	Cathodic protection
Friday		
Sept. 16—	9:00-11:30 a.m.	Chemical treatment

NACE HAS MOVED!

NEW ADDRESS

919 MILAM BLDG.

803 TEXAS AVE.

HOUSTON 2, TEXAS

NACE CALENDAR

NORTH EAST REGION—Board of trustees meetings scheduled September 22 and November 18.

METROPOLITAN NEW YORK SECTION—Meetings are scheduled Sept. 28 and Nov. 9, 1949; Feb. 8 and May 10, 1950.

PHILADELPHIA SECTION—Governing Board meetings scheduled August 1 and October 31. Section dinner meetings scheduled June 13, September 12 and December 12.

GREATER ST. LOUIS SECTION—Meets third Monday monthly. No meetings June, July, Aug., and September.

SHREVEPORT SECTION—Will hold no meetings during July and August. Regular meeting day is second Thursdays monthly.

TULSA SECTION — Meets Second Monday monthly.

NORTH TEXAS SECTION—Will hold its next meeting during September.

A. B. Campbell, Executive Secretary
National Association of Corrosion Engineers,
905 Southern Standard Bldg., Houston 2, Texas

I am interested in the SHORT COURSE ON CORROSION.
Please Send Official Registration Application to the Address Below:
(Print or typewrite plainly)

Name .....

Street .....

City..... Zone..... State.....

REGION REPORTS FOR 1948

Western Region's Annual Report was published in the February, 1949, issue.

NORTH EAST REGION

Following is the annual report of the North East Region as submitted December 28, 1948 by L. P. Donovan, secretary:

During the calendar year 1948 the North East Region held two meetings in conjunction with the local sections.

A luncheon and afternoon meeting held at the Philadelphia Engineers Club on December 2, 1948, was attended by approximately 100 members.

In New York on December 7, a dinner and evening meeting was held, attended by approximately 72.

There is considerable local interest in the two sections established in this region during the year. Each has a program of future meetings and has given considerable thought regarding subject matter to be presented.

Officers of these sections are: Metropolitan New York Section—W. E. Shaw, chairman; T. P. May, vice chairman; F. J. Le Febvre, secretary - treasurer. Philadelphia Section—H. L. Hamilton, chairman; A. V. Smith, vice chairman; E. R. English, secretary-treasurer.

It is hoped that during the year 1949 at least two more sections will be organized. These will probably be in Pittsburgh and Baltimore.

Officers of the region after January 1, 1949 are: E. P. Noppel, director; R. H. Lynch, chairman; N. P. Peifer, vice-chairman; L. B. Donovan, secretary-treasurer.

NORTH CENTRAL REGION

Chicago Section

The Chicago Section of NACE held six interesting meetings during the year 1948. These meetings started with a social hour from 6 to 6:45 p.m. in the lounge room at the Chicago Engineers Club. Dinner was served from 7 to 8 p.m. after which the meetings were opened.

Following are points of interest at the meetings:

January 15—"Laboratory, Field and Service Corrosion Testing," by C. L. Bulow of Bridgeport Brass Co.

February 19—"Resistance to Corrosion of Stainless Steel," by H. O. Teeple of International Nickel Co.

April 15—"Meeting Corrosion Problems in Vessel Fabrication," by J. O. Christenson of the Vessel Division, A. O. Smith Corp.

A nominating committee for the Chicago Section and the North Central Region was appointed.

May 20—"Potential Measurement in the Field," by William F. Croft, Standard Oil Co. of Indiana.

October 1—Joint meeting with the Electrochemical Society. Subject of discussion was "Description of Various Forms of Corrosion, Particularly from the Standpoint of Identification." Speaker was N. A. Luce, The Duriron Co.

Nov. 23—A conference session on "Corrosion Problems" with an open period for questions and answers was held with L. G. Vande Bogart of the Crane Company leading.

Attendance at meetings varied between 10 to 80 members and guests.

Chicago Section Officers for 1949 are J. P. Casey, chairman; V. J. Payton, vice-chairman; E. F. Jablonski, secretary; J. F. Kaszynski, treasurer.

Cleveland Section

Activities of the Cleveland Section for the year 1948-49 were as follows, according to the report submitted by E. W. Vereeke, secretary-treasurer:

The following meetings were held during the year:

March 25, 1948—Agenda included "Corrosion Resistance of High Nickel Alloys Including Stainless Steel," by F. L. LaQue, The International Nickel Co., Inc. and approval of by-laws and election of officers.

Sept. 20, 1948—Agenda included "Corrosion Problems in Two Industries," a panel discussion. C. Langdon Campbell, Diamond Alkali Co., "Corrosion in the Heavy Chemical Industry." E. W. Slathe, Standard Oil Company, "Corrosion in the Oil Industry."

Oct. 18, 1948—Agenda included "Corrosion Resistance of the New Carpenter #20 Alloy," discussed by Mssrs. B. T. Lanphier, Guba and Doughty of Carpenter Steel Co.

Nov. 22, 1948—Agenda included "Cathodic Protection of Hot Water Storage Systems," by Dan Fergus, research director of Cleveland Heater Co.

Jan. 24. 1949—Agenda included "Design and Fabrication of Corrosion-Resistant Process Equipment," by Everett C. Gosnell, Colonial Iron Works.

February 28, 1949—Agenda included "Metals and Corrosion." This was part of the corrosion course offered at the Stevens Institute of Technology.

March 28, 1949 — Agenda included "Hastelloy Alloys and Their Use in Combating Corrosion," by C. G. Chisholm, manager Hastelloy Department of Haynes Stellite Co.

Cleveland Section officers for 1948-49 were D. J. Connelly, chairman; H. H. Febrey, vice chairman; E. W. Vereeke, secretary - treasurer. Advisory Council: C. L. Campbell, Diamond Alkali Co.; George Heise, National Carbon Co.; F. E. Vandeveer, East Ohio Gas Co.; C. E. Dunasky, Harshaw Chemical Co.

The Regional Officers for 1949 are L. G. Vande Bogart, chairman; W. J. Sandel, vice chairman; R. A. Shoan, treasurer; N. E. Berry, director.

Considerable progress has been made toward organizing local sections in Milwaukee and Detroit.

EDITOR'S NOTE: The 1948 report of the Greater St. Louis Section was unavailable for publication with these summaries.

SOUTH EAST REGION

Activities of the Southeast Region during 1948 included two regional meetings, first held March 3 in Birmingham, Ala., with a one-day program. In the forenoon a series of field trips were made. In the afternoon four technical papers were presented as follows:

"Eight General Types of Corrosion Attack," by Dr. M. G. Fontana, Ohio State University; "Corrosion in Power Industry," by H. W. Cauthon, Georgia Power Co., Atlanta, Ga.; "Methods of Accelerated Paint Testing," by W. H. Abernathy, Southern Research Institute, Birmingham, Ala.; "Corrosion Prevention at Atlanta Water Works," by A. T. Storey, Atlanta Water Department, Atlanta, Ga.

Following a group dinner Dr. Ivy Parker, editor of Corrosion magazine, gave a brief review of the purpose and effectiveness of the publication. Mr. Tom Holcombe, Holcombe & Stearns, Shreveport, led a discussion on the aims and purposes of NACE.

On November 29 an afternoon and dinner meeting was held in Atlanta at which Dr. I. A. Denison, National Bureau of Standards, discussed the Bureau of Standards' soil corrosion test. An open forum was held on electrolysis and general corrosion problems.

SOUTH CENTRAL REGION

Activities of the South Central Region NACE and the local sections affiliated with it during 1948 were reported as follows:

Regional annual meeting held September 20-21 at Tulsa. Fourteen papers were heard by 261 registered. Officers were elected as follows: Nathan Schofer, chairman; A. L. Stegner, vice chairman; T. R. Statham, secretary-treasurer; M. C. Fleming, assistant secretary-treasurer.

West Texas Section

An inspection tour September 14-16 was conducted by the West Texas section with 112 registered.

Shreveport Section

Dinner meetings were held by the Shreveport Section on second Thursdays monthly except July, August and September. Average attendance was over 35. A barbecue held in November was attended by 125.

Corpus Christi Section

Ten dinner meetings were held during the year by the Corpus Christi Section. Average attendance was 25.

Tulsa Section

Excepting July and September Tulsa Section held monthly meetings. Nine papers were presented of which two have been recommended for presentation at the national conference in Cincinnati. Average attendance was 30.

North Texas Section

Eight meetings were held by North Texas Section, alternately in Fort Worth and Dallas. Attendance averaged over 20.

Houston Section

Seven meetings were held by Houston Section during the year, one of which was a joint meeting with ASME and another a luncheon conference with the Condensate Well Corrosion Committee. Attendance averaged 55, some coming from points as distant as Texas City, Freeport and Sulphur, La.

NEW PRODUCTS—Materials—Service—Literature

"Prufcoat Pruf Packet," a folder of filing size containing printed material giving detailed information about Prufcoat protective coatings, including an industrial price list and color chart is offered by Prufcoat Laboratories, Inc., 50 East 42nd St., New York 17, N. Y., to buyers of industrial paints. Detailed lists of services for which the coating is specifically recommended and tables giving characteristics in competition with other coatings is given.

The Rouy Photrometer gives concentration reading accurate to within 0.1 percent, according to E. Leitz, Inc., manufacturers, 304 Hudson St., New York 13, N. Y. Measured electrical energy is linear to transmitted light energy, the company claims. All adjustments are with a single control.

Dow Chemical Company has removed royalty fees from use of a plating process for magnesium developed a few months ago. The new license arrangement provides only that Dow be permitted free access to any process improvements which may be made by the licensee.

Accurate Humidity readings in confined spaces or in operating machinery are possible through use of a new motor-operated fan designed by Weston Electrical Instrument Corp., 617 Frelinghuysen Ave., Newark 5, N. J., for use with its Relative Humidity Indicator.

"National" Ground Anodes and Backfill Material for use in cathodic protection and electrical grounding is described in a new folder by National Carbon Co., Inc., Room 1328, 30 East 42nd St., New York 17, N. Y. Catalog Section M-8500A includes data on cathodic protection applications for pipe lines, water and gas mains, refinery equipment, underwater structures and structural footings: electrical ground connections for installations such as solvent tanks, automatic telephone exchanges, railway signal and lighting protection systems. New information is included on backfill materials and tables showing data to permit determining type, size and quantity of ground anodes and backfill required.

Backfill Type BF-2, which performs the function of furnishing an increased active surface to act as an anode for current discharge and lowering anode-to-soil resistance, thereby greatly prolonging the life of the anode by transferring electrochemical attack from the anode to the backfill, is described also.

"Banox," a Calgon, Inc., phosphate coating compound now is being used as a treatment to facilitate cold drawing of steel tube stock. The compound was used first as a lubricant in wire drawing. Calgon engineers discount a theory the coating aids in drawing processes because it forms an absorbent film which retains lubricant longer. They say the film is too thin for such action, explaining that Banox "plates out" on steel surfaces as an amorphous phosphate film, perhaps 15 millionths of an inch thick, and closely following the contours of metal surface.

"Neoprene-Coated" canvas gloves, curved to fit the hand, and designed for service with dangerous acids, caustics, chemicals and other irritants, now are being offered by B. F. Goodrich Co., Akron, Ohio.

Gerotor May Corp., Baltimore 3, Md., has published a new air valve catalog, Section 301, which gives details of new simplified Gerotor valves, design of which includes corrosion-resistant materials including bronze valve stem guide and valve lines.

"Penetrol" a Product of The Flood Company, Hudson, Ohio, is a material which stops rust without removing it, as a reinforcing reducer for paint and as a vehicle for aluminum paint. The company has several pieces of printed material describing uses of the vehicle, including methods of combining the material with other coatings.

Stephen D. Day has formed his own company serving the pipe line industry as national sales agent for the Ruberoid Company's pipe line asbestos felt. He also represents the Grip-Tite Manufacturing Company which manufactures the Stearns Grip-Tite pipe line anchor assembly used to hold down large diameter pipe lines, and is special representative for the Stearns Electronic Holiday Detector. The firm name will be S. D. Day Company and offices will be at 2017 West Gray, Houston 19, Texas.

"Rustnode," a magnesium anode designed to provide cathodic protection against rust scaling on condenser heads, dividers and tube sheets, supplementing water treatment for most economical protection, but also as sole protection in some instances, is being offered by Cathodic Protection Service, Houston, Texas and Tulsa, Okla. The anode, designed to protect only the walls of the chamber in which it is placed, may be used on fixed or floating heads. A plastic shielded mount allows current flow to be directed to useful protection, the company asserts, with little loss from overprotection of areas immediately adjacent. The ⅜-inch support rod for the anode is threaded for easy attachment, or may be welded to the plate.

Internal distribution and spacing of the anodes will be dictated by the size of the condenser and number of dividers. Life of the anode is affected most by water composition, current demand usually being proportional to total solids, the company says.

Paraline 18-8 Stainless Steel in solution is a new coating announced by the Barber-Webb Co., Inc., 8686 Rheem Ave., South Gate, Cal. Manufacturers claim corrosion-resistant qualities for the material, which consists of Type 302 stainless in a vinyl copolymer resin. It may be applied by spray, brush or dip over clean surfaces. No primer is required. It is recommended for outside oilfield and chemical plant equipment as well as many specialized applications.

Thirteen Kinds of stainless steel brushes carried as stock items by Osborn Manufacturing Co., Cleveland, Ohio. The many sizes and styles of brushes made by the company are recommended for a variety of uses. Included are two Ringlock types for jobs where scale and rust must be removed, which the company asserts may be run at speeds up to 20,000 rpm.

Heiline News, a periodical showing installations of various products of the Heil Process Equipment Corp., Cleveland 11, Ohio illustrates in its current issue numerous examples of pipe lining made by the firm.

"Piping Hot," a 22-minute 16-mm color motion picture showing the coating by stationary machines of 24-inch pipe and the laying of this pipe in an urban area now is available without charge for showing to interested groups. The motion picture, produced and offered by the Dearborn Chemical Company, can be booked by application to the Advertising Department, Dearborn Chemical Company, 310 S. Michigan Ave., Chicago 4, Ill. A booklet about the picture for audience distribution also is available and the company will appreciate receiving an estimate of the possible number in the audience so sufficient copies may be provided.

PERSONALS

Frank C. Lipscomb, will serve as special representative of Dearborn Chemical Company in the promotion of railroad cleaners.

Eric G. Skarin has been named service metallurgist by the Ohio Ferro-Alloys Corp., Canton, Ohio. He has had wide experience in steel melting and processing with Bethlehem Steel Company and Midvale Company.

Ralph H. Hunter, Midland, Mich., has been made a member of the board of directors of Dow Chemical of Canada, Ltd., along with Calvin A. Campbell and Donald Williams.

James T. Gow has been named chief metallurgist for Electric Steel Foundry Co., Portland, Ore., producers of steel castings and specialty equipment.

Vice President L. E. Osborne of Westinghouse Electric Corp., Pittsburgh, Pa., has been given staff supervision over all the company's manufacturing activities, including production and industrial relations. James H. Jewell, recently elected vice president, has assumed staff responsibility for all sales and marketing.

Corrosion Problems

QUESTIONS

No. 27—Bakelite (phenolic resin) washers are used to insulate specimens in laboratory and plant corrosion tests. What is the limiting temperature above which decomposition of the resin and corrosion by such decomposition products may be expected?

No. 28—What material can be used for air piping in the aeration of sewage (containing up to 2000 ppm of organic matter; up to 6 ppm of oxygen and up to 15 ppm of carbon dioxide)?

No. 29—What material or materials can be used for electrical conduits and other electrical wiring accessories in sewage disposal plants where there is exposure to moisture laden air containing hydrogen sulfide?

QUESTIONS AND ANSWERS

No. 9—(February, 1949). How is the corrosion resistance of wholly austenitic stainless steel (Types 304 and 316) and related materials, in the form of castings, affected by variations in the condition of the exposed surfaces e.g., machined vs. sand blasted vs. shot blasted vs. electropolished, etc.?

ANSWERS

Smooth, polished surfaces offer maximum corrosion resistance. Rough surfaces actually mean more initial attack due to greater surface area exposed. When this rough surface is corroded away, little difference is expected in corrosion rate.—Anonymous.

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It is the popular impression that the condition of exposed surface does affect the over-all corrosion experienced on a casting especially when there is an appreciable corrosion rate. For instance, the more uniform the surface, the less corrosion experienced, due to the reduction of the total exposed surface area. This is especially true of the stainless alloys which often depend upon the formation of a "passive" film on the surface which affords its protection. This film is less easily broken if the surface is smooth and uniform. However, the use of special surface preparation often is not practicable from the economic standpoint and its use must be considered separately for each situation.—W. A. Luce.

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Since stainless steels are subject to pitting in environments which attack them appreciably, it is always desirable to eliminate any surface imperfections which could tend to pit formation. Hence, a machined surface that eliminates all surface imperfections could be superior to an electropolished surface (over a rough cast surface) which might not close a sand hole.

Shot blasting is not suitable as it introduces a foreign, more corrodible material into the surface of the stainless alloy.—W. E. Pratt.

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No. 10—(February, 1949). What evidence has been accumulated to determine whether graphitic and/or metallic wire woven packing materials are responsible for corrosion of steel pump shafts due to galvanic action? What regularly available packings do not cause or affect the corrosion of shaft materials either in storage or during stand-by conditions or while the pump is in service?

Questions and Answers for this section should be submitted to L. G. Vande Bogart, Crane Co., Engineering and Research Division, 836 S. Michigan Ave., Chicago, Illinois. All questions will become property of NACE. Those not printed will be answered by mail. Questions should carry sufficient detail to describe the problem. Answers to printed questions are solicited. Authors of questions will remain anonymous to readers, while authors of answers may remain anonymous by request.

ANSWER

We have no data on wire woven packings. Graphitized packings may cause galvanic corrosion on most any shaft material, especially during idle periods if the electrolyte is suitable. However, much of the reported corrosion from this source could be largely due to service corrosion.

During the war, pumps were shipped overseas on decks of vessels where salt spray could get into packed stuffing boxes. In one case where stuffing boxes were specified to be packed at the factory with graphited asbestos packing over Monel shaft sleeves, such serious corrosion occurred on the Monel sleeve in 6 months time, before pumps reached their destination and were installed, that all sleeves had to be replaced.

Recently the writer saw a FA-20 shaft sleeve from a pump handling weak HNO_3, where graphite from the packing was adhering to the sleeve. Underneath the spots or "rings" of graphited material, corrosion was definitely observed.—W. E. Pratt.

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No. 14—(March, 1949). The "Langlier Index" is used as an index of the corrosivity of natural or treated waters at normal temperatures. What is the effect of increasing temperature on the reliability of this index? Can the "Langlier Index" be used to indicate the probable corrosivity of domestic hot water (above 140° F.) with particular reference to galvanized storage tanks and/or copper tubes in indirect hot water heaters?

ANSWER

"The 'Langlier Index' *predicts* the formation of a carbonate deposit from water. The protective value of this carbonate barrier depends on its physical nature and adherence to the metal, i.e., whether and to what extent it will exclude water. Besides this and temperature, there are several other factors such as dissolved oxygen, turbulent flow and contact effects that tend to cause pitting unless the carbonate deposit is fully protective. If the deposit is protective at normal temperature and it is not disturbed by temperature changes and the composition of the water is practically the same, it probably will afford protection at higher water temperatures.[1]

Evidently the practical application of this index is not as simple as it may seem to be. Graphs indicating the pH—alkalinity relations to produce a uniform thickness of $CaCO_3$ between 80° and 150° F. are available."—F. N. Speller.

1. Corrosion Handbook, John Wiley & Sons, Inc., New York, 1948 (See references p. 502).
2. Powell, S. T., Bacon, H. E., and Knoedler, E. L., *Industrial Engineering Chemistry*, Vol. 40, No. 3, 453-457 (1948).

No. 18—(March, 1949). Is there any serious acceleration of corrosion when coupled galvanized and stainless steel sheets are exposed in the atmosphere? Is the trend in the same direction in all types of atmosphere; e.g., urban, industrial, marine?

ANSWERS

Although quantitative information is lacking, it is not believed that there will be any serious acceleration of corrosion when coupled galvanized and stainless steel sheets are exposed in the atmosphere. There might be a slight tendency in urban and industrial atmospheres for those areas of the galvanized sheets which are adjacent to the stainless steel to be attacked slightly more than would be the case of uncoupled sheets. This attack would be accelerated slightly more in marine atmosphere. In extreme cases where the sheets might be moist due to sea spray all or a great portion of the time, the accelerated attack on the galvanized steel might be noticeable, but the fact that water tends to collect in droplets and not continuous films would tend to reduce the galvanic attack—Anonymous.

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Our own experience indicates that galvanic corrosion of Zn in contact with 18-8 stainless steel in marine-industrial atmosphere (New York City) is approximately the same as when coupled with cold rolled steel. While we do not have data of this type of galvanic corrosion in rural and marine atmospheres, we'd expect zinc to corrode at about the same rate as when it is coupled with ordinary steel. ASTM data indicate that zinc coupled with both Type 304 and 316 Stainless steels corrodes worst in New York and least at State College, with Kure Beach somewhere in between. Our data check ASTM's New York data fairly closely.—K. G. Compton.

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No. 22—(April, 1949). What is the mechanism of zinc chromate inhibition when used in metal primers?

ANSWER

Zinc chromate is slightly soluble in water. The chromate ions formed when a zinc chromate primer is wet with water react with the metal surface converting it to a thin layer of highly insoluble metal chromate. Presumably those areas which are most anodic are first chromated, followed by the lesser anodic areas in turn until the surface is substantially coated. Electrode potential measurements of the chromated surface show it to be passive—passivity being the result of anodic polarization.—R. M. Burns.

Do You Have A CORROSION PROBLEM?

If you do you are invited to submit it to the editor of this section for an answer by persons who have met a problem similar to yours and have found solutions.

1949 NACE DIRECTORY SUPPLEMENT

Following Is An Alphabetical List of NACE Members Added Since Publication of the Directory in January

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Corrosion Abstracts

BEARING

High-Temperature Greases. H. A. McConville, General Elec. Co. *Product Eng.*, **19,** No. 1, 93-95 (1948) Jan.

Factors to consider when selecting and applying greases for high temperature service include stiffness, dropping point, acidity, evaporation, effect of different metals on oxidation, and operating speed. Rate of oxidation of a grease that is in contact with bearings fitted with bronze retainers is three to four times that of ordinary steel. Ordinary naval brass and aluminum bronze speed oxidation; stainless and rustless steels are somewhat better. One of the most stable surfaces is chromium plate. —INCO.

COATINGS

Vinylite Resins Combat Corrosion and Fouling. *Marine Eng. & Shipping Rev.*, **53,** No. 5, 82 (1948) May.

New system for combating corrosion and fouling consists of a novel wash primer pre-treatment for the metal, an anti-corrosive primer and an anti-fouling coating, all based on vinylite resins, which have properties of unusual toughness, adhesion, and chemical resistance. Vinylite resins dry to tough film in 30 min. and are insensitive to normal dry-dock conditions. Developed by Bakelite Corp.—INCO.

D.D.T. as a Marine Anti-Fouling Agent. J. F. Marchand. *Prev. Det. Abs.*, **4,** Lac 20 (1948).

The properties of DDT, especially its water-insolubility and lipoid solubility, are those desirable in an anti-fouling agent. A series of experiments to test its anti-fouling properties showed it to be effective for barnacles, but not effective in the control of other marine fouling organisms. After four months it had not been leached out by sea-water. It does not adversely affect drying properties or durability. The addition of DDT to normal anti-fouling paints containing copper, etc., is suggested.—RCLPI.

Application of Organic Coatings to Galvanized Iron Surfaces. R. Mansell. *Painter and Decorator*, **61,** 6-9 (1947); **62,** 4-8 (1948). *Z.D.A. Abs.*, **6,** No. 6, 86 (1948).

A discussion of the difficulties of securing good paint adhesion on hot-dipped galvanized surfaces and of methods used to overcome the difficulties.—RCLPI.

Protective Packaging. M. Lewis. *Prod. Fin.*, 1, No. 1, 26-33 (1948).

A proprietary packaging process is described which consists of: 1) masking and taping with pressure-sensitive tape, 2) spraying with a cobwebbing lacquer, 3) building up a thick layer of clear protective lacquer film, 4) blowing out solvent vapors from the package and 5) coating with either a thin coat of aluminum-pigmented bitumen or a heavy coat of a bitumen mastic according to storage conditions. The coating can be scraped off when necessary.—RCLPI.

Acid-Resisting Lacquers and Varnishes. A. Kufferath. *Metalloberflache*, **1,** No. 6, 140-141 (1947).

K. reviews the composition, properties and applications of lacquers and varnishes suitable for the protection of metal surfaces against acidic liquids, vapors, and gases.—MA.

Anodizing and Dyeing Magnesium Alloys. Anon. *Internat. Ind.*, **29,** No. 4, 169 (1948).

A process for the anodic oxidation of magnesium alloys, similar to the anodizing of aluminum is described. If in addition a sealing coat of zinc chrome primer, followed by suitable top coats, is given to the anodized metal, 2000 hrs. salt spray is required to break down this protection system.—RCLPI.

Service Trials of Painting Schemes Applied to a Steelworks Gantry. J. C. Hudson. *J. Iron Steel Inst.*, **159,** 60 (1948); *J. Brit. Shipbuilding R. A.*, **3,** No. 7, 325 (1948).

The results of practical painting trials on a steelworks gantry are described and compared with those of parallel small-scale outdoor exposure tests. Both agree in showing that the efficiency of protective painting schemes applied to steel is greatly increased by removing the mill scale by pickling before applying the paint. In small-scale tests, the average life of two-coat painting schemes on pickled steel exceeded 7 years, as compared with 1½ years for steel prepared by weathering and hand-cleaning. The procedure of coating the steel with linseed oil while still hot after rolling also was tried. The results proved better than those for weathered steel but inferior to those for pickled steel, because the mill scale left beneath the paint ultimately gave rise to cracking or local failure of the paint film. Differences between the performance of the various painting schemes tested were generally of secondary importance compared with those associated with differences in the surface preparation of the steel before painting.—RCLPI.

Abstract Section Style Outlined

For ease in locating reference data, CORROSION uses a uniform style in its Abstract Section.

The abstracts first are broken down into major classifications of the more common types of corrosion literature. In each review the title of the article is presented in bold face type, followed by the author's name. The publication from which the article was abstracted is printed in italics and is abbreviated in most instances. Following this, in sequence, are the volume (bold face), number in the volume, pages, year and month of publication. In some instances a second reference will be listed in the same manner. This indicates that the article also was published or abstracted in another publication. A brief summary of the article follows the above information and it is concluded with an abbreviation indicating the source of the abstract and contributor. The meanings of these abbreviations usually are listed on the first page of the Abstract Section.

When seeking more detailed data about an abstract, best source of information is the publication in which the article appeared originally. (Listed in italics in the heading.) The contributor of the abstract also may be able to supply additional information. Addresses of most of these publications may be found in the reference section of most public libraries.

Abbreviations at the end of abstracts indicate source of abstract and contributor; and are as follows:

AER	*Aeronautical Review*, Institute of Aeronautical Sciences, Inc.
ALL	*The Abstract Bulletin*, Aluminum Laboratories, Ltd.
AWWA	*Journal*, American Water Works Association
BLR	*Battelle Library Review*, Battelle Memorial Institute Library
BNF	*Bulletin;* British Non-Ferrous Research Association
CALCO	Calco Chemical Division, American Cyanamid Corp.
CE	*Chemical Engineering*, McGraw Hill Publishing Co.
CEC	Consolidated Edison Co. of New York, Inc.
EW	*Electrical World*, McGraw Hill Publishing Co.
GPC	General Petroleum Corp. of California
INCO	The International Nickel Co., Inc.
IP	Institute of Petroleum
MA	*Metallurgical Abstracts*, Institute of Metals, London, Eng.
ME	Marine Engineering
MR	*Metals Review*, American Society of Metals
NALCO	National Aluminate Corp.
NBS	National Bureau of Standards
RA	*Refrigeration Abstracts*, American Society of Refrigeration Engineers
RM	*Revue de Matallurgie*, Paris, France
RPI	*Review of Current Literature Relating to the Paint, Colour, Varnish & Allied Industries*, Research Association of British Paint, Colour & Varnish Manufacturers, London.
TDD	*Technical Data Digest*, Air Materiel Command—Technical Service Section
UOP	Universal Oil Products
No Code	*Current Technical Literature*, Bell Telephone Laboratories

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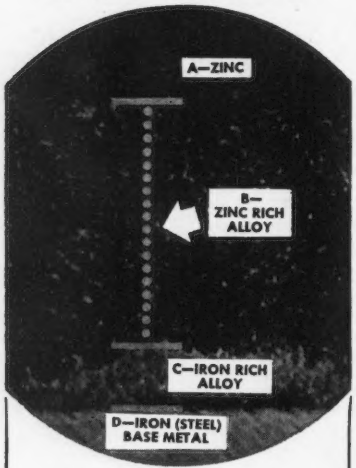

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hot-dip GALVANIZING

Some Metallurgical Aspects of Electrodeposits. (I, II.) Carl E. Heussner, A. R. Balden, and L. M. Morse. *Plating*, **35**, No. 6, 554-561+; No. 7, 719-723, 768 (1948).

The structure of deposits of various types and from a number of typical plating baths is described. The relationship between hardness and crystal size is discussed, together with the effect of inclusions on hardness. Tensile strength and brittleness of deposits are considered and methods of determining them briefly outlined. Work done by various investigators on the determination of internal stress in deposits is reviewed and the nature of adhesion dealt with. The relationship between the various physical characteristics mentioned and the appearance, corrosion-resistance, and fatigue life of the deposits is examined.—MA.

Modern Anti-Corrosive Paints. Hubert Hesse. *Metalloberflache*, **1**, Nos. 11/12, 261-262 (1947).

A review of the developments necessitated by the German war economy.—MA.

Protective Pipe Coating Used on Underground Lines. *Heating, Piping & Air Conditioning*, **20**, No. 7, 194 (1948).

Protective pipe coating "Duratex" is resistant to electrolysis, corrosion and shock, impact, ductility, and high flash and fire points and is not affected by alkalis and soil acids. Mfd. by Nat. Petroleum Sales, Inc.—INCO.

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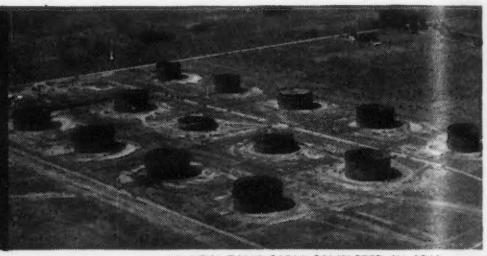

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Why Paintwork Blisters. Anon. *Decorator*, **47**, No. 556, 50-2 (1948).

A general discussion of blisters on painted wood work, covering the role of trapped air and moisture, resin exudations, oily under-coats, and surface preparation.—RCLPI.

Organic Finishes for Increasing the Life of Bus and Truck Parts. R. B. Davis. Soc. Automotive Eng, Preprint *Z.D.A. Abs.*, **6**, No. 3, 40 (1948).

Recommendations are made on suitable undercoats and top coats for use on the various metals found on commercial vehicles. A zinc chrome primer should be used on all aluminum alloys subject to corrosive conditions. Zinc and cadmium plating of steel help to reduce electrolytic corrosion in contact with aluminum. Subsequent phosphating and priming provide a further safeguard. Some notes are included on the adhesion of paint to zinc.—RCLPI.

Protective Coatings. L. A. Critchfield. *Prod. Fin.*, **30**, (1948) Mar. *Plastics* (London), **12**, No. 134, 346 (1948).

A review covering synthetic resin finishes, etc.—RCLPI.

The Protection and Finish of Pressed Steel Kitchen Equipment. W. F. Coxon. *Sheet Metal Inds.*, **25**, No. 249, 122-124 (1948) Jan.

Due to the corrosive atmosphere of the kitchen, preventive measures, such as, properly cleaning, passivating, phosphating, painting and inhibitions must be taken on steel kitchen furniture, refrigerators and washing machines.—INCO.

Stainless Steel Base for Paint. *Chem. & Eng. News*, **25**, No. 20, 2924 (1947) Oct. 6.

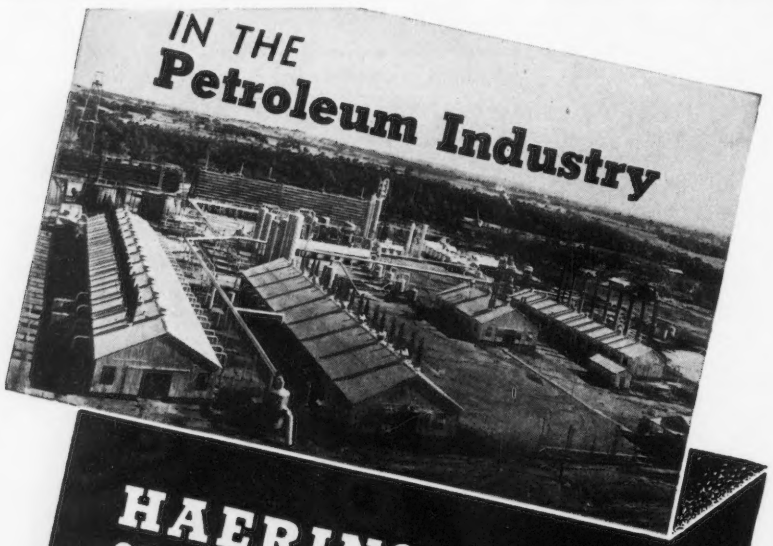
A number of paint manufacturers are engaged in testing the physical qualities of stainless steel powder-base paint, the material being furnished in a paste form, which when mixed with any commercial vehicle such as lacquer, will render a surface highly resistant to such corrosive conditions as those caused by nitric, phosphoric or sulfuric acid fumes. Reports show that the working life of the painted surface is increased as much as 300 percent. Stainless steel powder-base paint, using a spar varnish or lacquer vehicle, is available from Chas. Hardy, Inc.—INCO.

Sprayed Zinc. *Chem. Age*, **57**, No. 1485, 815 (1947).

Zinc spraying of a bus body is claimed to increase its service life.—MA.

Tropicalisation Studies. Centro Research Labs. U. S. Bureau of Ordnance (Navy Dept.), Reports Nos. 29-31, 1946-7; *Prev. Det. Abs.*, **4**, F. 35-41; 1948, cf. Review, 331 (1948).

Salicylanilide in p-phenylphenolic resin vsh. (at a concn. of 11.3%), ethyl cellulose lacquer (8.75%) and cellulose acetate-propionate lacquer (15.0%) was found to be a fungicide effective against test moulds Phenyl-mercuric-o-benzoic sulphimide proved an effective fungicide when incorporated into vinyl wire coatings or insulations. Neither zinc dimethyldithiocarbamate or a naphthenate soln. (67% total solids) and metallic zinc (8%) was effective. Fungistatic phenolic plastics were prepd. by mixing



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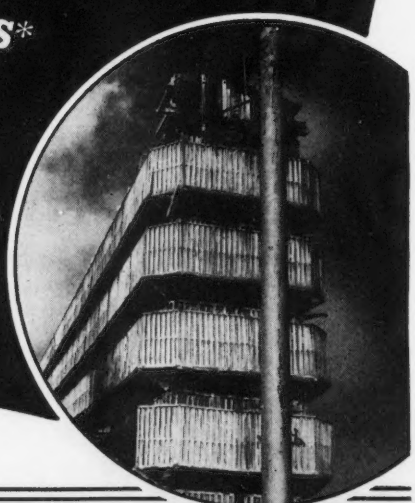

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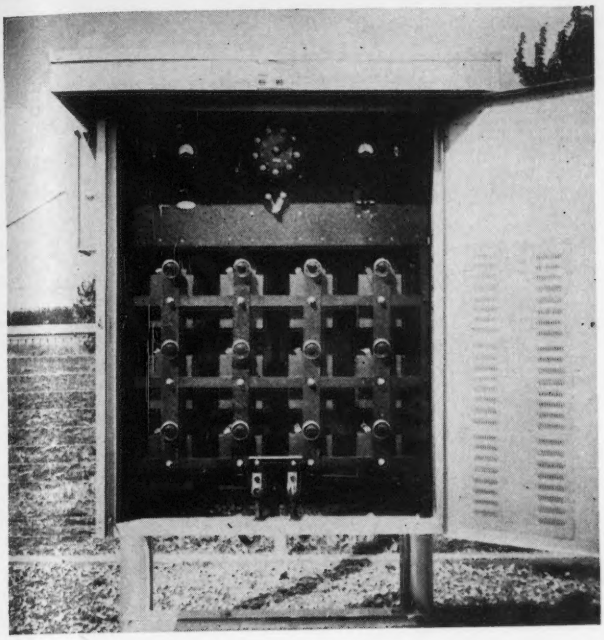

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5% of a concentrate containing 50% of a mercurial fungicide in hydrogenated castor oil (used as a mould lubricant). Rubber accelerators used in original coatings did not prove fungistatic. Fungicidal varnishes containing up to 15% salicylanilide were prepared for selenium rectifiers (where coatings free from mercury are required), but showed a tendency to bloom.—RCLPI.

Zinc Contamination: Methods of Purification of Bright-Nickel Plating Solutions. H. D. Carter. *Metal Ind.*, **72**, No. 9, 170-173 (1948).

The dark deposits that occur in low c.d. areas in Mazak die-castings are known to be due to zinc contamination. Several methods are available for the purification of plating solutions. C. carried out investigations on both precipitation and low-c.d. methods. With the former, using nickel carbonate, he increased the zinc concentration from the usual 40-45 p.p.m. to about 80 p.p.m., and varied the pH. He concludes that separation of zinc is virtually complete at pH 6.8, but that a considerable part of the nickel is also lost, while the nickel: cobalt ratio remains const. He recommends a pH of 6.3-6.6 for the purification. The Liscombe method, using ferrous sulphate, was found to be unreliable. Tests on the low-c.d. method showed that zinc is most efficiently removed at low c.d., but more quickly at high c.d. In general, low-c.d. treatment is far more efficient and reliable than precipitation treatments, but the latter are recommended where there is serious contamination and rapid treatment is essential.—MA.

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Painting a Jack-Knife Bridge. Anon. *Can. Paint & Var. Mag.*, **22**, No. 4, 14-6 (1948).

The bridge, which required about six tons of paint, was cleaned and descaled with oxy-acetylene flame before painting. All paints, including zinc chrome/iron oxide primer, undercoat and finish, were applied by spray.—RCLPI.

Rheem Puts Galvanizing on Conveyor Line to Make Its Welded Water Tanks. *Business Week*, No. 98, 66-67 (1948) July 31.

Picture story of how a galvanized welded water tank is made at Rheem Mfg. Co.—INCO.

Surface Protection of Steel by Cladding with Copper. Hans Broking. *Metalloberflache*, **1**, No. 5, 101-104; No. 6, 137-139 (1947).

After a brief review of the various methods of coating steel with copper, the production of copper and copper-alloy clad steel by rolling is described. The importance of making a clean bond between the coating and the steel base is emphasized, and methods of adhesion testing are outlined. Copper cladding improves the thermal and electrical conductivity of the steel, but decreases the average tensile strength to an extent depending on the relative thickness of coating and base. The chemical resistance is the same as that of copper, provided that damage to the coating is avoided and cut edges are not allowed to come into contact with corrosive liquids or gases.—MA.

Deposition of Nickel and Cobalt by Chemical Reduction. Abner Brenner and Grace E. Riddell. *Proc. Amer. Electroplaters' Soc.*, 156-169; discussion, 169-170 (1947). *Met. Abs.*, **15**, 414 (1948).

A description of work carried out by the U. S. National Bureau of Standards on immersion deposits of nickel, cobalt and nickel-cobalt alloys.—MA.

Nickel Plating by Chemical Reduction. J. G. M. Brenner. *Nature*, **162**, 183-184 (1948) July 31.

Outlines proposed mechanism for the method described by Brenner and Riddell.—BLR.

Corrosion Resistance of Air-Dried Butyl Titanate Film. C. R. Bowes and G. Winter. *Paint Notes*, **3**, No. 4, 114-17 (1948).

Butyl titanate which had been treated with sodium in butyl alcohol to reduce its chlorine content to 0.003% and then pigmented with aluminum, showed good corrosion resistance when placed in a humidity cabinet. Corrosion resistance is related to chlorine content of the butyl titanate. It is possible to produce a butyl titanate of very low chlorine con-

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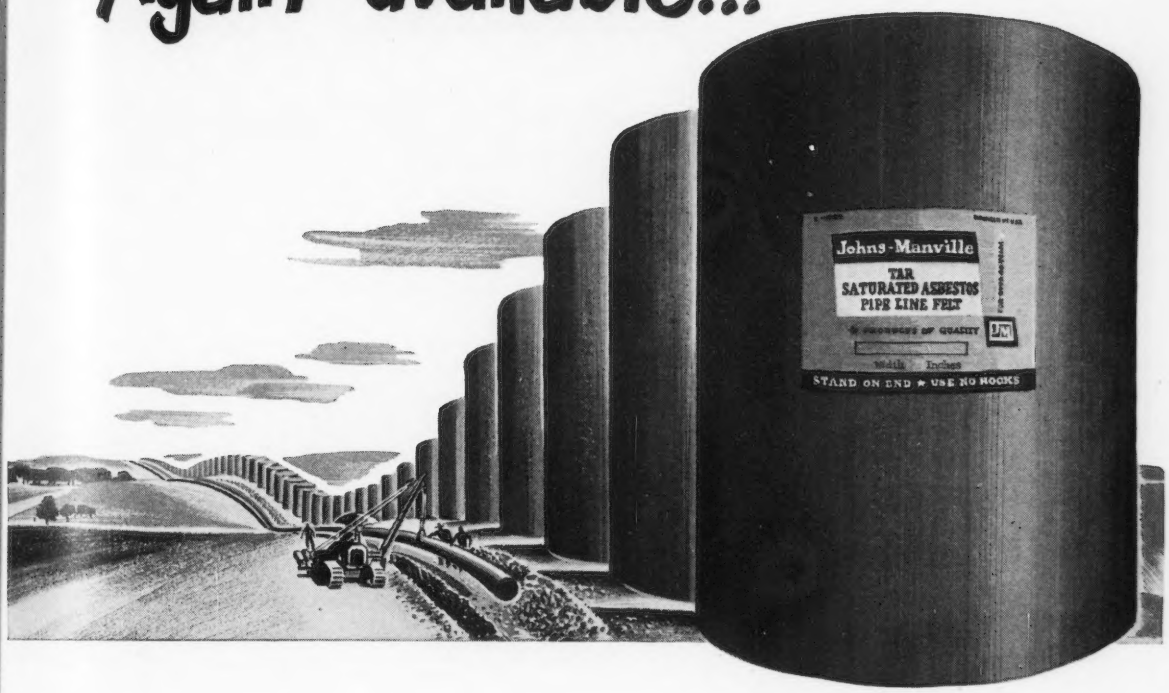

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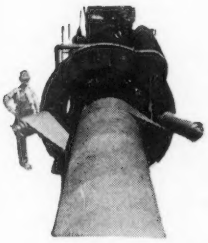

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tent by a modification in the usual method of manufacture.—RCLPI.

Durability of Colored Exterior Enamels. E. C. Botti. *Off. Dig.*, No. 279, 367-8 (1948).

Exterior enamels formulated with alkyd vehicles improve in durability as the pigt. vol. concn. is increased from 5% to 15%. Suggestions are made as to pigments to be used for various colored enamels for exterior use, e.g., mixtures of phthalocyanine blues or greens with zinc chromates may replace Brunswick greens where resistance to alkali or H_2S is required.—RCLPI.

Protective Coatings. R. B. Grossman. A.G.A., Comm. on Heat Treating and Finishing with Gas, Industrial & Commercial Gas Sect. *Ind. Gas*, **26**, 12 (1947) Dec. *Metals R.*, **21**, No. 1, 28 (1948) Jan.

An evaluation of seven commercial coating materials used to prevent oxidation or decarburization of steel surfaces during heat treatment.—INCO.

Rust Is Not Inevitable (Flame Spraying with Zinc or Aluminum). H. W. Greenwood. *Prod. Fin.*, **1**, No. 4, 42-49 (1948).

A description of the flame spraying of iron and steel surfaces with zinc or aluminum, using the powder pistol.—MA.

Importance of Proper Control in Anodizing Aluminum Alloys. Allen G. Gray. *Prod. Fin.*, **12**, No. 10, 78, 80+ (1948).

The effect on the properties of anodic films of alloy composition, concentration and temp. of electrolyte, c.d., and time of treatment, is considered.—MA.

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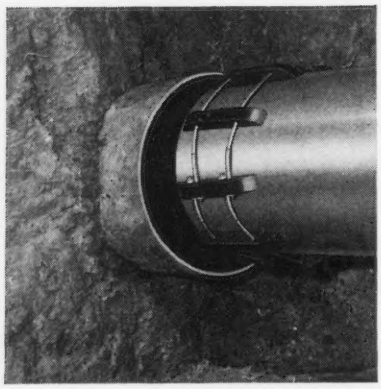

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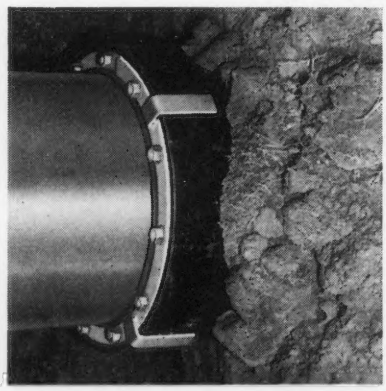

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Red Lead and Zinc Chromate in Anti-Corrosive Paints. J. Frydlender. *Rev. Prod. Chim.*, **49**, No. 5/6, 40-1 (1947). *Z.D.A. Abs.*, **6**, No. 6, 92 (1948).

A comparison of the rust-preventing properties of red lead and zinc chrome. The author reports some American experiments on the water absorption and permeability of paints containing the two pigments, and concludes that red lead functions by keeping water from the metal surface, whereas zinc chrome acts by allowing water to extract soluble chromates which then inhibit corrosion. Alkyd resin vehicles are used with zinc chrome because of their own impermeability, which prevents too rapid exhaustion of the soluble chromates. There are also notes on barium K chromate and chromated red lead.—RCLPI.

Use of Zinc Yellow or Zinc Chromate for Protection (of metals) Against Corrosion. J. H. Frydlender. *J. Iron Steel Inst.*, **158**, 406 (1948). *Brit. Abs* B-II, 261 (1948).

Recent progress is reviewed.—RCLPI.

Protective Coatings—Their Composition, Properties, and Applications to Brewery Equipment. H. W. Foelsh. *Brewers' Digest*, **22**, No. 9, 67-70 (1947); *Chem. Abs.*, **42**, No. 4, 1436c (1948).

The compn., properties, and application of protective coatings to brewery equipment are discussed in detail.—RCLPI.

Pigments, Metallurgy. W. L. Borrows and Others. Off. Tech. Serv. Report PB. L 86699; N.P.V.L. Abs., No. 137, 159 (1948).

Three targets were visited and anti-fouling paints and infra-red paints on ships for anti-radar work are mentioned.—RCLPI.

Cuprous Oxide Anti-Fouling Paint. II—Inactivation of Highly Pigmented Films Containing Metallic Copper. R. L. Benemelis and Others. Off. Tech. Serv. Report PB. L78676, 34 pp. (1947). N.P.V.L. Abs., No. 134, 85 (1948).

For paints intended for application to steel, metallic copper pigments should be avoided at concns. > 25% pigment volume.—RCLPI.

Action of Rust-Preventive Oils. E. R. Barnum, R. G. Larsen, and A. Wachter. *Corrosion*, **4**, 423-431 (1948) Sept.

Summarizes results of certain experiments on the above, including details of apparatus and procedure. Proposes a mechanism for the protective action of oil solutions of polar compounds on steel. Illustrated. 12 ref.—BLR.

The Adsorbed Layer as a Passivating Factor. (In Russian.) G. S. Koshurnikov. *Zhurnal Obshchei Khimii* (Journal of General Chemistry), **18**, No. 80, 388-397 (1948) Mar.

Adsorption of phenol from aqueous solution onto iron, zinc, iron oxide, and aluminum oxide was investigated. Surface layers resulting from the adsorption are irreversible, indicating the character of the reaction is chemical and possesses a certain thermal and chemical stability vs. weak acids. This stability may be "fixed" by condensation with formaldehyde or urotropine.—BLR.

Insecticidal Surface Coatings. S. S. Block. *Soap*, **24**, No. 2, 138-41+; No. 3, 151-3; No. 4, 155-61+ (1948).

Data are presented to show the effec-

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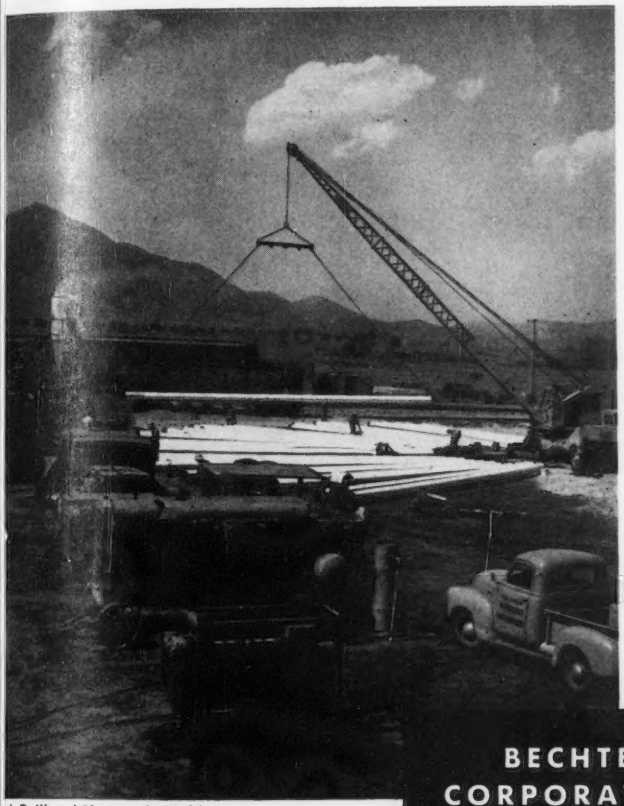

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tiveness of a number of insecticides, including DDT, benzene hexachloride and pyrethrum, in a number of coating media. Generally, oil-containing coatings produced with DDT had poor insecticidal qualities. The incorporation of pigments improved the results. A urea/formaldehyde resin was outstanding but plasticizers usually reduced its effectiveness. Age improved the coatings and the formation of surface crystals of DDT was demonstrated in a number of cases. A coating containing DDT and asphalt was shown to renew its surface deposit after it had been repeatedly wiped down. The continued deposition is attributed to gradual pptn. from a supersaturated solution.—RCLPI.

FUNDAMENTALS

Exchange Between Copper Foil Tagged with Radio-Active Copper and a Solution of Copper Ions. (In French.) Pierre Sue, Marguerite Quintin, and Marie Bizouard. *Compt. Rend.* (France), **226**, 1723-1725 (1948) May 24.

Outlines preliminary results from a study of the above. The number of atomic layers or depths of the metal surface participating in the exchange varied from 500 to 17,000, depending on the method of preliminary surface preparation. The results should be of great value in metallography.—BLR.

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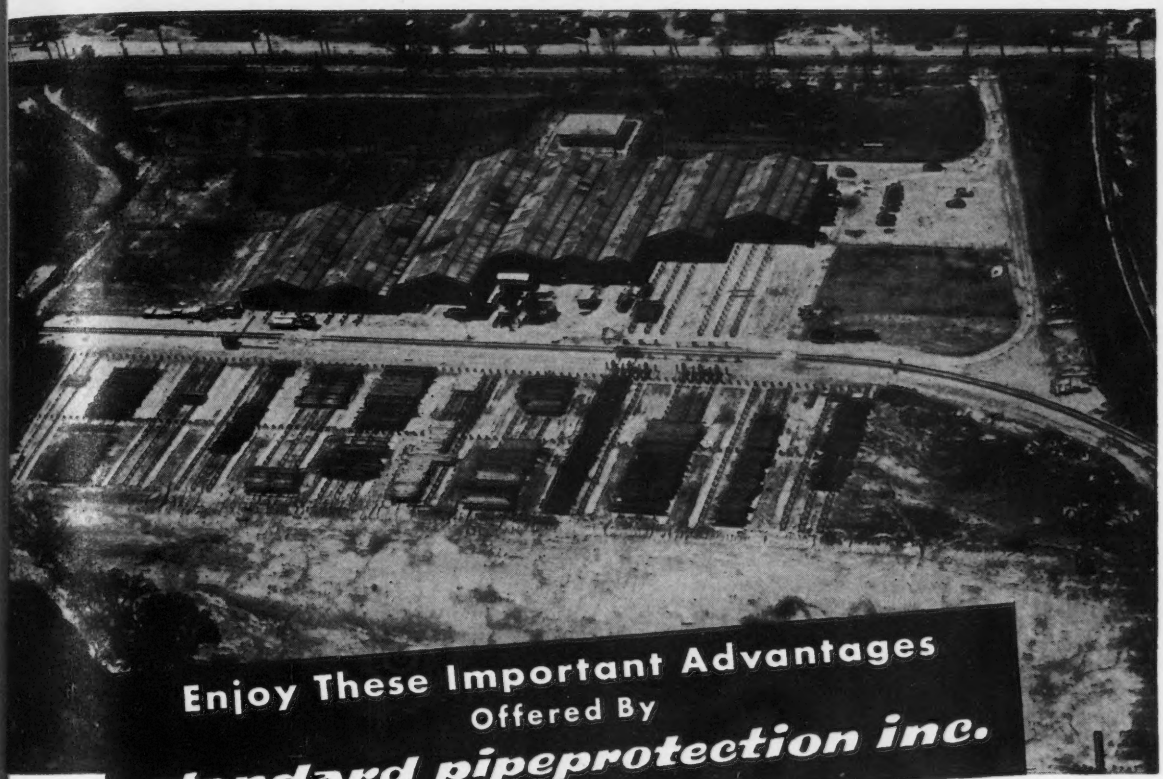

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On the Formation and Analysis of Electrolytic Oxide Films on Aluminum and Anticorodal. Fritz Liechti. Thesis E.T.H. Zurich, 68 pp. (1947).

In unagitated 10% sulphuric acid as electrolyte and at a c.d. of 0.01 amp./cm.^{2} the anodic oxidation of aluminum proceeds in such a way total thickness of the specimen and the film thickness increase linearly with time, rising to a maximum after four hours. On further treatment total thickness decreases linearly while film thickness remains constant. In agitated solutions similar effects occur but the maximum takes place after three hours. Pure aluminum, refined aluminum, and Anticorodal all have similar properties to a greater or lesser extent. The thickest film is obtained with refined aluminum. It is clear, therefore, that after the maximum film thickness has been attained, film goes into solution from the electrolyte-film interface at the same rate as new film is formed at the film-metal interface. In 0.16 M-oxalic acid as electrolyte and at c.d. of 0.01 amp./em.^{2} total thickness of the specimen and the film thickness increase linearly with time but do not reach a maximum even after five hours, i.e., there is no noticeable solution of the film. During the oxidation the ratio film thickness: increase in total thickness of the specimen remains constant. In sulphuric acid solutions the ratio is 1.5-1.55, and in oxalic acid solutions 1.85-2.0; the film thickness can be determined, therefore, at any stage of the oxidation by multiplying the increase in total thickness by this factor, and this is of great practical importance. In the sulphuric acid process the SO_3 content of the film is dependent on the time of oxidation and is 13.4 and 11.25% after one hour in unagitated and agitated solutions, respectively, but after five hours the constant value of 8% is obtained in both cases. The absorbed water is ¼% in sulphuric acid films and only 0.5% in oxalic acid films; this explains the inferior dyeing properties of the latter. The oxalic acid process films contain 3% of oxalate. In both types of film the combined water is 5-6%. This corresponds to a film formula of $3Al_2O_3.1H_2O$ in the oxalic acid process, but in the sulphuric acid process a third to a half of the combined water goes with the SO_3. so that, according to the time of oxidation, the films have the composition $9Al_2O_3.1SO_3.2H_2O$ to $6Al_2O_3.1SO_3.H_2O$. Studies show that the thermal oxidation of aluminum is not noticeable at 350° C. and only occurs to any appreciable extent above 600° C. It proceeds more slowly in damp air than in dry air or oxygen because, in the presence of moisture, the film is more compact, less porous, and has fewer fissures. When electrolytically polished in perchloric acid-acetic anhydride the reflectivity of aluminum rises sharply to 83% after four minutes treatment and then increases slowly to a maximum of 86% after 10 minutes. The polishing process can be modified to strip intact oxide films from the basis metal. L. critically reviews suitable methods which can be employed for the various determinations made at every stage of the investigation. The colorimetric determination of small amounts of aluminum by eriochromcyanin-R is best conducted at pH 3.8 and after standing for 3-4 hours, when the color remains constant. The ether-hydrochloric acid method is suitable for the determination of aluminum oxide in aluminum, and by slight modification it can be adapted to stripping the oxide film. In both cases the metal is dissolved and the oxide left untouched. The ether-aluminum chloride complex formed can be separated, purified, and, by distillation at 147° C. under 11 mm. of mercury, obtained as colorless crystals with m.p. 36° C.; they have the const. composition $AlCl_3.(C_2H_5)_2O$ and the structural formula

$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!O; \quad \begin{matrix} Cl \\ Al\text{-}Cl. \\ Cl \end{matrix}$$ —MA.

Intercrystalline Corrosion of High-Purity Aluminum as Influenced by the Nature of the Grain Boundaries. (In French.) Paul Lacombe and Nicolas Yannaquis. *R. de Metallurgie*, 45, 68-76; discussion, 76-77 (1948) Mar.-Apr.

Discusses the mechanism of the above on the basis of the literature and of experimental results, which latter are illustrated by photomicrographs. Both chemical and electrochemical attack were investigated. The usual explanation based on the presence of impurities is not valid for the very pure aluminum dealt with. It was found that the amount of attack varies in accordance with grain-boundary contour, which can be explained on the basis of more or less void volume. 17 ref.—BLR.

A Rapid Method of Preparing Single Metallic Crystals (of Aluminum). Paul Lacombe and Louis Beaujard. *R. Met.*,

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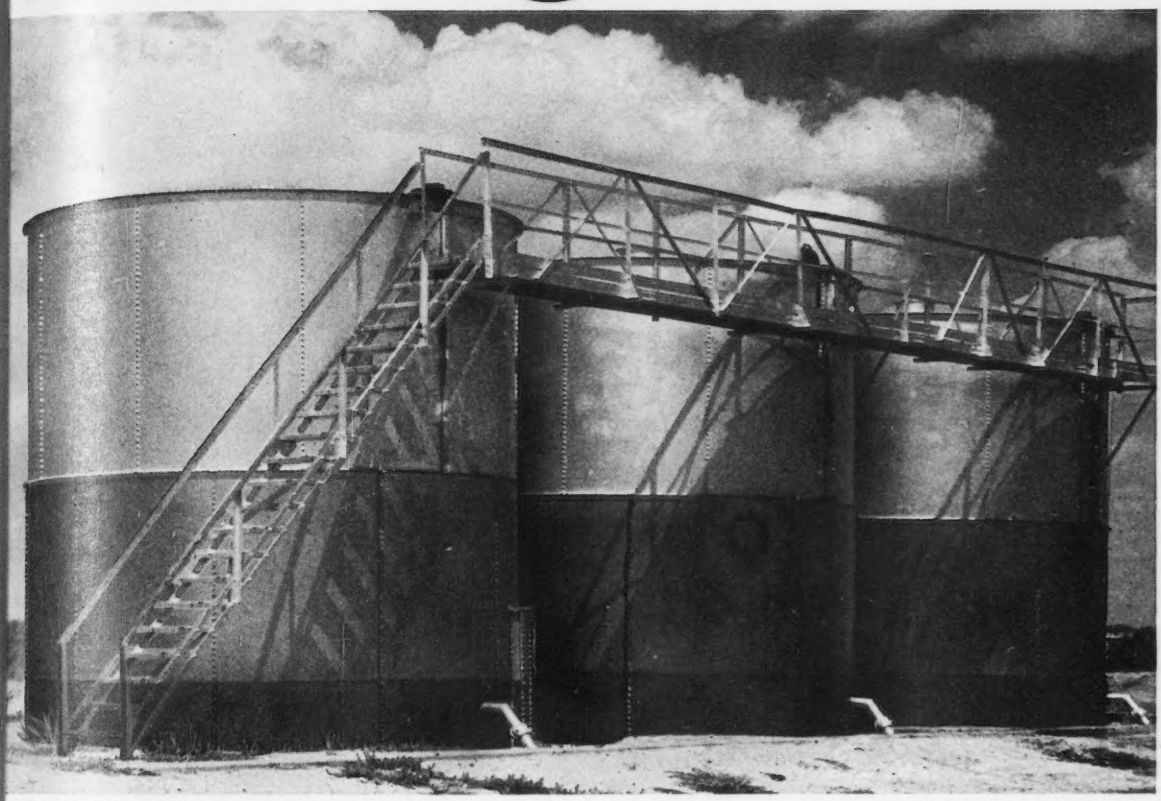

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44, Nos. 3/4, 65-70 (1947). Read before the Société Française de Metallurgie.

The classical methods of preparing single crystals are reviewed and a method of doing this by solidification with surfusion of 99.99% pure aluminum, using special precautions to keep out foreign inclusions, is described. A piece of aluminum sheet, about 15 x 10 cm. and 1-3 mm. thick, is heated to about 700° C. on a clay slab in an electric muffle furnace with a temp. gradient of 10° C. between its two ends. The plate melts but is held to its shape by the oxide skin. The temp. is then lowered at the rate of about 100° C. in 15 min. The aluminum supercools and suddenly solidifies from the cooler edge, forming about once in three times a single crystal. By this means L. and B. studied the effect of work-hardening on extra-pure aluminum and the effect of traces of impurity on grain-size. This method is much more rapid than other means of producing single crystals and is superior to them for studying work-hardening, because of the difficulty with which aluminum is work-hardened and of its tendency to recrystallize at ordinary temp., the more rapidly the greater the purity of the metal.—MA.

The Growth and Structure of Thin Oxide Films on Aluminum. (In German.) Georg Hass. *Zeitschrift fur Anorganische Chemie,* **254,** 96-106 (1947) Sept.

Electron diffraction, the electron microscope, and Drude's polarization method were used to investigate the thickness and structure of the above films and the effect of temperature on the rate of oxidation of aluminum. Electrolytically produced aluminum oxide foil was found to change at 700° C. from the amorphous into the crystalline state. Data are charted and tabulated and several X-ray diffraction patterns are shown. 12 ref.—BLR.

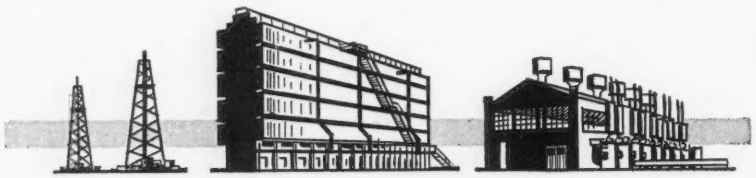
Application of Electron Diffraction Techniques to the Study of Corrosion Processes. E. A. Gulbransen. *Corrosion,* **4,** No. 9, 445-455 (1948) Sept.

The nature of the protective or non-protective corrosion films on metals and alloys has been studied by electron diffraction and electron microscope methods. The use of such refined methods has been necessitated because in the protective range, the corrosion films are of the order of 10 to 10,000 angstroms in thickness. The article shows the relationship of the electron diffraction and the electron microscope technique through a general study of the dry oxidation surface reaction. The problem is broken down into three groups of study, the first of which is concerned with the kinetics or the rate of reaction and in what manner this rate is influenced by time, temperature, pressure, surface factors and chemical factors in the gas atmosphere. The second class of studies is concerned with the structure factors which include the crystal structure, primary structure and secondary structure. In the thin film range, the crystal structure is obtained from an analysis of the electron diffraction pattern ring diameters and line intensities and a comparison with X-ray data. The primary structure or crystal size and shape may be estimated from the width of the diffraction lines and the spot structure of the diffraction ring. The third class of factors include: 1) the atomic composition or chemical analyses of the film, 2) the lattice defects and impurities in the film, 3) the mechanism of the reaction.

The electron diffraction camera in use at the Westinghouse laboratories is shown schematically. The apparatus consists essentially of a source of homogeneous high voltage electrons of 30,000 to 60,000 volts energy, a magnetic focusing coil, a sample holder and manipulator, a camera section, and pumps for maintaining the vacuum. The camera includes a fluorescent screen by which the electron pattern can be made visible and a photographic film which permanently records it. To reduce the scattering of electrons the apparatus is evacuated continuously by a series of pumps to a very low pressure. To obtain a good pattern by the reflection technique the samples must be plain, crystalline and somewhat abraded. The surface preparation is important. Usually the specimens are abraded flat with various grades of polishing paper, using kerosene as a lubricant. If it is necessary to study the behavior of the specimens at high temperatures, they can be mounted in a furnace and studied in any gas atmosphere and at the temperature of interest. Methods of study and results are given for oxide films on iron and chromium. —ALL.

Intercrystalline Corrosion of Aluminum Alloys. A. I. Golubev. *J. of Phys. Chem. (U.S.S.R.),* **22,** 591-601 (1948). *Chem. Absts.,* **42,** No. 18, 6731 (1948) Sept. 20.

Duraluminum contains grains of $CuAl_2$. Crystals of $CuAl_2$ (ϕ phase + small inclusions of n phase; copper 54.9



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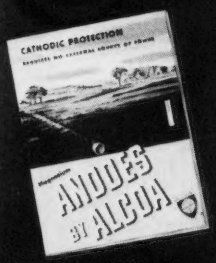

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The Electrochemical Theory of the Solution of Metals in Acids. IV. (In Russian.) Ya. V. Durdin. *Zhurnal Obschei Khimii* (Journal of General Chemistry), **18,** No. 80, 345-363 (1948) Mar.

Gives details of a theoretical, mathematical analysis of the cathodic and anodic processes and their relative influences on the interaction of metals with acids. Typical curves are charted. 17 ref.—BLR.

The Zone of Metal Phase Consumption in Gas-Metal Reactions. Andrew Dravnieks and Hugh J. McDonald. *J. of the Electrochem. Soc.*, **94,** 139-151 (1948) Oct.

Shows, by an analysis of the scale-growth process, that the scale formed in the reaction between gas and metal must consist of at least two layers formed by some secondary process, for example, recrystallization. The concept of a uniform process of scale growth is, therefore, an oversimplification and fundamentally incorrect. This conclusion is supported by results of an investigation on copper iodide scale. Protective-film formation on aluminum and the accelerated growth of oxide films on metals at the beginning of oxidation are explained on the basis of these considerations.—BLR.

Selective Surface Oxidation of an Alloy and the Influence of Metal Structure on the Course of Dry Oxidation. (In French.) Pierre Chevenary and Xavier Wache. *Revue de Metallurgie,* **45,** 121-128 (1948) May-June.

Gives details of an experimental investigation of the above for a 5.2%-chromium nickel alloy; for a 2.4%-aluminum, 2.4%-manganese aluminum alloy; for a 49.5%-nickel ferronickel; and for an 18-8 stainless steel. A thermomagnetic method and the thermo-balance were used to follow the course of oxidation. It was found that during dry oxidation, the diffusion of metal into the surface layer is blocked by an oxide film. Physical and chemical transformations in this film take place during the first hour of heating. Charts and photomicrographs.—BLR.

Dry Corrosion Investigated at Pittsburgh Conference. *Chem. Eng. News,* 26, No. 26, 1901 (1948).

A report on the Pittsburgh International Conference on Surface Reactions held at the Mellon Institute, 6-11 June 1948. Very brief summaries are given of papers dealing with the oxidation of copper and zinc, the preparation of large single crystals of metals, and the effect of temp. on the electrode potential of zinc.—MA.

The Surface States and the True Physicochemical Properties of Metals. (In French.) Georges Chaudron. *Revue de Metallurgie,* **45,** 61-67 (1948) Mar.-Apr.

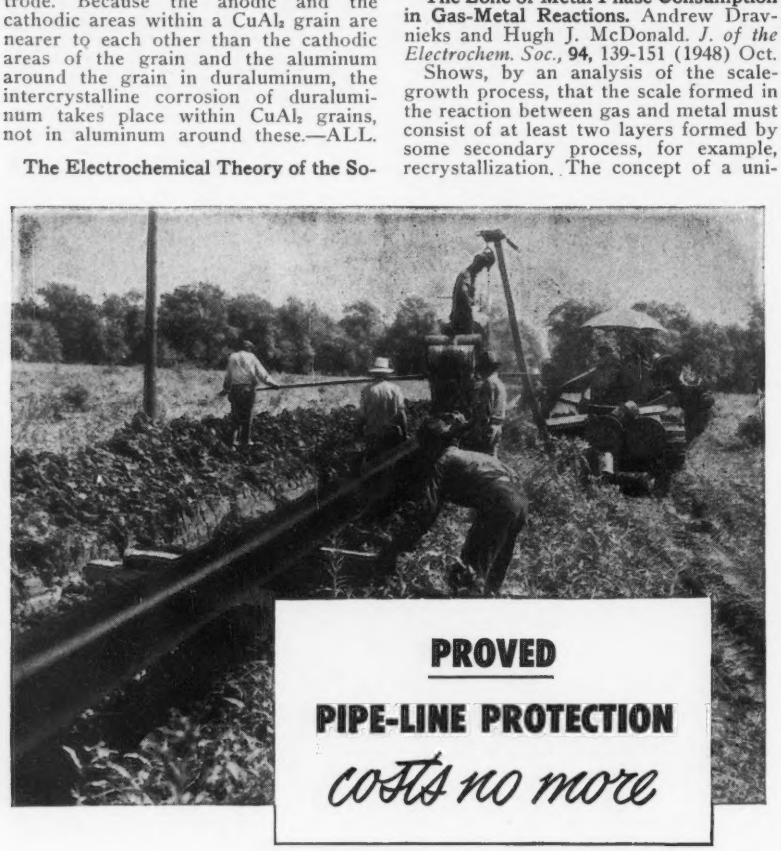
The rate of attack of corrosive media on metals depends primarily on the nature of the oxide film and secondarily on the structure of the upper layer of metal. However, investigations showed that other factors are involved (effects of which have not as yet been fully established) which may be of even greater importance in the physicochemical behavior of metals. 11 ref. —BLR.

Oxidation of Aluminum at Low Temperatures. (In French.) N. Cabrera. *Revue de Metallurgie,* **45,** 86-92 (1948) Mar.-Apr.

Proposes a theory of oxidation at low temperatures and gives results of experiments mostly at room temperature, but also a few at temperatures up to 450° C., in which very thin films of aluminum, prepared by vacuum deposition on glass, were exposed to dry oxygen, dry ozone, ultraviolet irradiation, moist air, and moist oxygen. Optical factors of the films (transmission and reflection) were measured before and after exposure, as these have been found to have a direct relationship to the degree of oxidation. The method, which is described, is not satisfactory at elevated temperatures. The composition of the oxide layer under different conditions is discussed. Data are charted. 14 ref.—BLR.

Corrosion by Concentration Cells. *Corrosion Reporter* (International Nickel Co., Inc.), **3,** 1-7 (1947) Nov.

Discussion of fundamental causes of concentration-cell corrosion, the mechanism of corrosion of this type with



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INDEX TO ADVERTISERS
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Vol. 5 No. 7

	Page
Allied Chemical & Dye Co. (Barrett Div.)	vii
Aluminum Company of America	23
American Cast Iron Pipe Co.	14
American Hot Dip Galvanizers' Assoc., Inc.	10
American Pipe & Const. Co.	Inside Front Cover
Bechtel Corp. & H. C. Price Co.	17
Cathodic Protection Service	18
Cathodic Servicing Co.	13
Corrosion Engineering Co.	12
Crose, M. J., Mfg. Co.	25
Dowell, Inc.	ii
Electro Rust-Proofing Corp.	18
General Paint Corp. (Hill, Hubbell Div.)	26
Haering, D. W. & Co.	12
Heil Process Equipment Corp.	25
Huddleston Engineering Co.	18
International Nickel Co., Inc., The	viii
Johns-Manville	15
Koppers Co., Inc.	24
Mavor, James E. Co	20
Mayes Bros., Inc.	i
Midwestern Engine & Equip. Co.	v
Minnesota Mining & Mfg. Co.	21
Mutual Chemical Co.	22
Natasco Co.	10
National Carbon Co.	vi
Perrault Brothers	11
Pipe Line Service Corp.	x
Plastic Lining Corp.	18
Rosson-Richards Co.	18
Service Engineers, Inc.	ix
Sims, C. I.	18
Standard Pipeprotection, Inc.	19
Stearns, D. E.	Back Cover
Tator, Kenneth	18
Thayer, Starr	18
Williamson, T. D.	16

typical examples, and the means for its prevention.—INCO.

Corrosion of Iron and Steel; Atmospheric Protection and Marine Fouling. *Metallurgia*, **38**, 201-206 (1948) Aug.

Presents summaries of papers on protection against atmospheric corrosion, anti-fouling compositions, cementiferous paints, and accompanying discussion at a recent meeting of the Iron and Steel Institute and the British Iron and Steel Research Association.—BLR.

Corrosion of Metals Research; Progress Report of the Chemical Research Laboratory. *Metallurgia*, **38**, 282-285 (1948) Sept.

Extracts from recently published report record progress made in the fields of organic inhibitors and microbiological corrosion.—BLR.

Corrosion of Metals. Its Cause and Prevention. F. J. Maffei. *R.A.E.; Bol. da Repart. de Aquas e Esgotos* (Sao Paulo), **9**, 52-73 (1947) Aug. *Public Health Eng. Abstr.*, **28**, No. 6, 31 (1948) June.

A survey is presented of existing knowledge covering the electrochemical corrosion theory of Whitney and Walker, electrode potentials, the electrochemical series, polarization, and local electric elements due to different metals or concentrations of oxygen. The passivity of steel, cobalt, nickel and chromium in different solutions, and the service of nonmetallic, soluble metallic, and noble metallic coatings are described. Noble metallic coatings require a perfect pore-free cover. Soluble coatings like zinc can become anodic at 60° C. and then increase corrosion. (No more information in abstract.)

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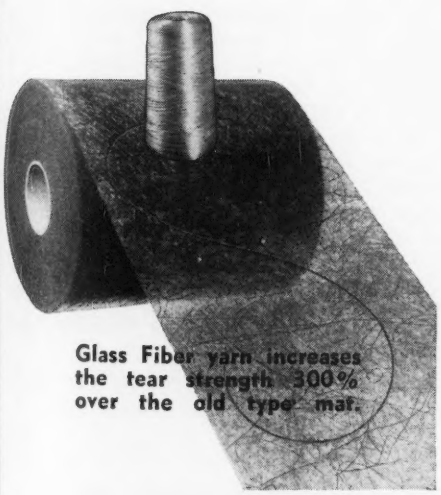

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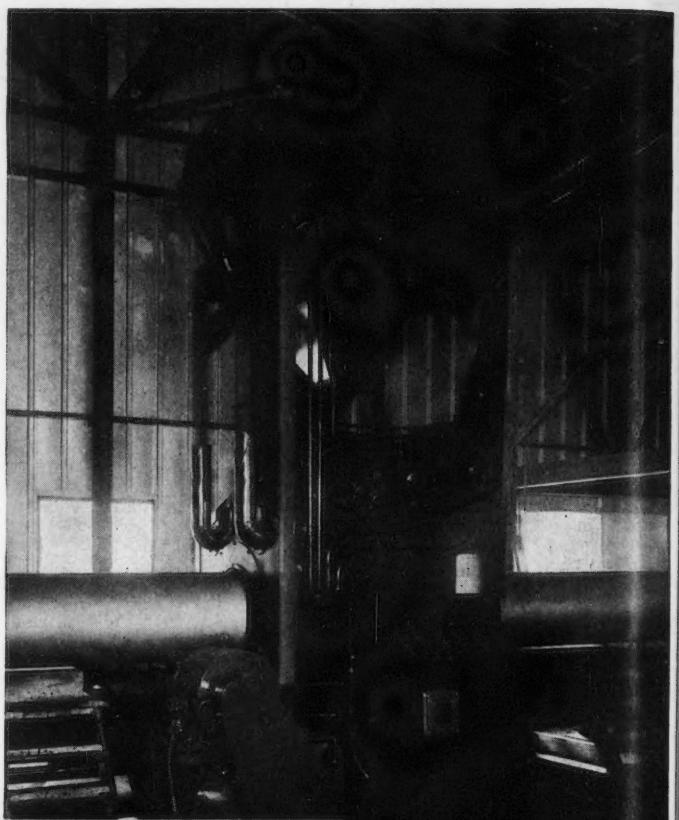

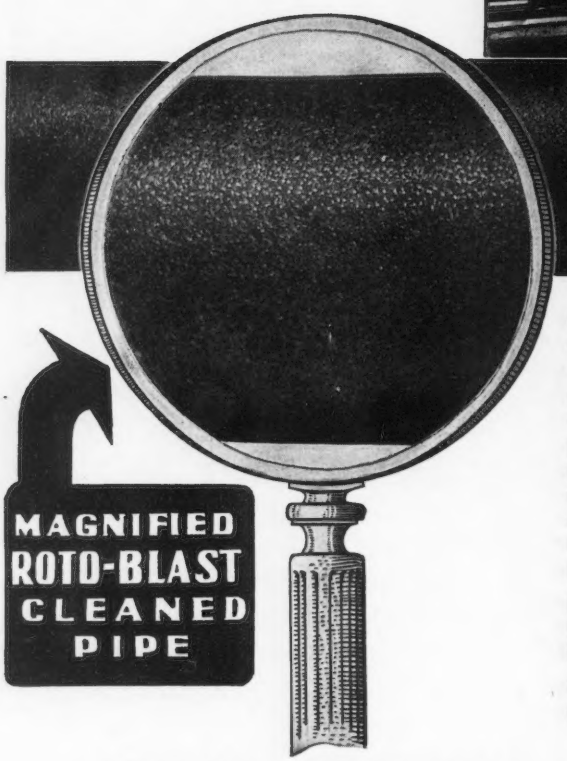

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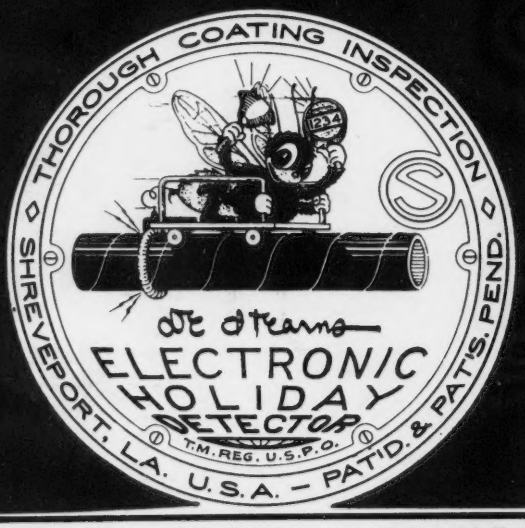

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